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PROBABILISTIC CONSEQUENCE ASSESSMENT OF HYDROGEN SULPHIDE RELEASES FROM A HEAVY WATER PLANT: ADDENDUM AND SUMMARY

by

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PROBABILISTIC CONSEQUENCE ASSESSMENT OF
HYDROGEN SULPHIDE RELEASES FROM A HEAVY WATER PLANT

ABSTRACT

This report provides a summary of work carried out on behalf of the Atomic Energy Control Board, concerned with the consequences of accidental releases to the atmosphere of hydrogen sulphide (H_2S) at a heavy water plant. In this study, assessments of consequences are made in terms of the probabilities of a range of possible outcomes, i.e., numbers of fatalities, given a certain release scenario.

The report describes the major features of a computer model which was developed to calculate the consequences and their associated probabilities, and the major input data used in applying the model to a consequence assessment of the Bruce heavy water plant (HWP) in Ontario. The results of the sensitivity analyses of the model are summarized. Finally, the results of the consequence assessments of 43 accidental release scenarios at the Bruce HWP are summarized, together with a number of conclusions which were drawn from these results regarding the predicted consequences and the factors which influence them.

RÉSUMÉ

Le présent rapport résume les détails d'un travail effectué pour le compte de la Commission de contrôle de l'énergie atomique au sujet des conséquences des rejets accidentels dans l'atmosphère d'hydrogène sulfuré (H_2S) provenant d'usines d'eau lourde. L'étude fournit des évaluations de conséquences en terme de probabilité de certaines répercussions possibles, comme le nombre de fatalités en fonction d'un scénario de rejet donné.

Le rapport décrit les principales caractéristiques d'un modèle informatique qui a été mis au point pour évaluer les conséquences et leur probabilité, ainsi que les principales données d'entrée à employer pour appliquer le modèle à une évaluation des conséquences de l'usine d'eau lourde de Bruce (Ontario). Le rapport résume les résultats des analyses de sensibilité. Il résume aussi les résultats des évaluations de conséquences de 43 scénarios de rejets accidentels à l'usine d'eau lourde de Bruce, de même que les conclusions qui ont été tirées de ces résultats concernant les conséquences prévues et les facteurs qui les influencent.

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A. INTRODUCTION

Heavy water (deuterium oxide) is an essential material in the Canadian nuclear industry, since it acts as both moderator and coolant in the present generation of CANDU reactors. Although heavy water occurs naturally in water bodies, it is found in such low concentrations that the required quantities and purity for reactor use must be obtained by an extensive separation process.

In Canada, this process is carried out in heavy water plants employing the Girdler-Sulphide method. Operating plants are currently located at a site in Bruce County, Ontario. The Girdler-Sulphide process employs large quantities of hydrogen sulphide (H_2S), a highly toxic chemical, which is recognized as a potential hazard to both the work force and the general public in the vicinity of the plants. Although extensive precautions and contingency plans are in place to minimize the risk of exposure to injurious levels of H_2S, further study of this question is important to both operators and regulators as they seek to further reduce this risk.

The study summarized in this report was undertaken to assist the Atomic Energy Control Board (AECB) in the licensing of heavy water plants by significantly extending the existing techniques of safety assessment. At present, licensees are required to report on the effects of possible process failures on members of the public. In the case of H_2S releases to the atmosphere, this is normally done by calculating the downwind concentrations of the gas under a range of weather conditions, based on H_2S emission rate expected from a postulated break size in the pressure envelope. A number of break sizes, or initiating events, are considered. The resulting gas concentrations are compared with an assumed safe level. The assessment of the acceptability of the risk is then a judgement made by the AECB. The work described herein now permits a quantitative assessment of risk, assuming that the postulated accident occurs. Results are expressed in terms of the probabilities of certain consequences, i.e. numbers of casualties, recognizing that the effects on the public of a given event would vary significantly, depending on such factors as gas release conditions and the local wind and weather at the time of the accident. This is termed a probabilistic consequence assessment, to distinguish it from a full risk assessment, which also takes account of the likelihood of the postulated initiating event occurring.

This report provides a summary of the complete consequence assessment work programme carried out on behalf of the AECB. The work programme was conducted in five phases and is described in detail in four earlier reports, plus an addendum which appears as an appendix to this report. The scopes of the earlier reports were as follows:

Scope Determination (Ref.1)

In the first report, the nature of the problem of consequence assessments of H2S releases was discussed and analyzed in detail, including consideration of the initial blowdown of gas from various pipe breaks and storage tank ruptures, the behaviour of the gas cloud immediately downstream of the rupture, subsequent atmospheric dispersion phenomena and the toxicity of H2S and sulphur dioxide (SO2). Critical factors were identified and the specifications for a computer model to perform such assessments were set out, with special reference to the Bruce heavy water plant site. The framework for the computer model was recommended, as well as detailed terms of reference for its implementation.

GASPROB Code Documentation (Ref.2)

The computer code GASPROB was subsequently developed according to the recommendations of Ref. 1 and is documented in the second report. The code includes mathematical simulations of initial gas behaviour, such as gravitational settling of a heavier-than-air release and the rise of jets and flares, subsequent atmospheric dispersion under a range of possible weather conditions, and the toxic effects on the exposed population. The code makes use of the site-specific dispersion climatology, topography and population distribution, and probabilistic lethal dose data for the released gas (H2S or SO2). Output for a given initiating event can be provided in the form of ground level gas concentrations around the point of release, projected numbers of fatalities within specified areas and the projected total fatalities regardless of location, each with an associated probability. GASPROB is presently written in ASCII FORTRAN for use on a Digital Equipment VAX 11/750.

Consequence Assessments (Ref.3)

This report includes the numerical results of a series of sensitivity studies carried out on the GASPROB code to determine the dependence of the code output on certain input parameters and assumptions implicit in the program. The report also gives the results of 43 full consequence analyses specific to the Bruce heavy water plant (Bruce HWP), encompassing a range of postulated pipe break sizes and H2S storage tank failures, assumed release heights and plant operator actions to control the release (by process tower isolation and dumping of its contents to a flare stack). Ignition or non-ignition of the H2S are also included in the range of scenarios. Statistical experimental design was applied in the selection of scenarios and analysis of variance of the results was carried out to identify significant factors and combinations of factors.

Sensitivity Study of SO2 Toxicity (Ref.4)

This study investigated the sensitivity of the probabilistic consequences projected by GASPROB to changes in the assumed toxicity of SO2. The results provide an estimate of the likely "error band" of consequence probabilities due to this sensitivity for a large, burning release of SO2 simulated in earlier work.

In the present report, a summary is first provided of the methodology used in the consequence assessments (Chapter B). This includes an outline of the various components of the GASPROB model, a review of the major input data assembled for this study (i.e., topographic, climatological and population data, as well as the gas release rates calculated for the various initiating events), a summary of the sensitivity analyses which were conducted on the model and the selection of events for full consequence assessment by GASPROB. The results of the sensitivity analysis and consequence assessments are summarized in Chapter C. The major conclusions and recommendations drawn from the study are given in Chapter D. As an appendix, a recent review of the literature on the acute toxicity of H2S is given. This second review (an earlier review was completed on behalf of the AECB in 1981, Ref. 5) concentrated on the literature published in the last five years to determine if any new data would modify or substantiate the conclusions of the earlier report and

which were the basis of the H2S toxicity model used in GASPROB.

A second appendix gives changes to the first report (Ref.1) which arose from a peer review by Ontario Hydro, together with a discussion of the effects on the consequences predicted by GASPROB due to these changes.

B. METHODOLOGY

1. General Description of Model

The overall methodology adopted for the consequence assessments of H2S releases from heavy water plants involves, firstly, the postulation of an initiating event, i.e., a certain quantity of H2S or SO2 released to the atmosphere over a given time and at a given location. The second component is concerned with the route to the receptor followed by the gas once it is released, according to such factors as the wind and weather conditions. Finally, the response of the receptors to the resulting downwind gas concentrations is determined in a collective sense, i.e., as a function of the population density in the affected area. For a given release, or initiating event, the consequence is expressed in terms of a probability distribution of the number of casualties.

In the first phase of this work, a review was undertaken of the Girdler-Sulphide process and the distribution of the H2S inventory at the Bruce HWP (see Ref. 1). From this information, potential gas release scenarios were identified for simulation by the model. This was done without a detailed assessment of the credibility or likelihood of such events. However, by taking a broad view of possible initiating events, the model was designed to handle the full range of cases which, at some later date, if not at present, may be considered worthy of a detailed consequence assessment. These include burning or non-burning releases from pipe breaks and manway failures, liquid H2S storage tank and tank car failures, breaks in lines carrying liquid H2S and dumping of H2S to a flare stack.

Depending on the initiating event, there are a number of possible mechanisms of release of H2S or S02 to the atmosphere. These mechanisms will affect the initial gas behaviour and its dispersion in the atmosphere. This, in turn, affects the concentrations received downwind. The initial gas behaviour which results from the various release mechanisms was reviewed in detail in Phase 1 of this programme, together with the mathematical models available to simulate such behaviour (see Ref. 1). These were incorporated into the GASPROB code, allowing the simulation of such effects as the rise of a jet of gas, buoyant plume rise due to a burning release or flare of H2S, the "lift-off" of a buoyant release at ground level, the initial gravitational settling and spreading of a heavier-than-air gas cloud and then its transition to normal dispersion behaviour, and the aerodynamic effects of plant structures on gas dispersion. Gaussian plume and puff dispersion equations are then used to predict subsequent atmospheric dispersion and downwind gas concentrations at ground level, depending on wind and weather conditions. GASPROB includes a terrain adjustment option to simulate the effect of topographic relief on ground level concentrations, and an optional lakebreeze dispersion model. The code also simulates the indoor/outdoor effect, in which the peak concentrations experienced inside a building can be lower than those experienced outdoors at the same location.

The portion of the GASPROB code dealing with receptor response is based on a statistical "peak-to-mean" model developed earlier for the AECB (Ref. 5). This model predicts the probability of short-term lethal concentration peaks of H2S (or S02). In GASPROB it is used to derive the overall probability of all possible combinations of lethal concentration and exposure time at a given receptor. Several lethal concentration-exposure time relationships must be input to the model, e.g., LC50, LC10 functions (lethal concentrations for 50% or 10% of the population). This results in a probability distribution of the number of fatalities at a given receptor, or model grid element, based on the population resident in the grid element. GASPROB then adds up the results for all grid elements to produce a probability distribution for the whole area under study. A further addition of consequence probabilities is performed for the range of possible wind and weather conditions, each condition being weighted according to its relative frequency of occurrence. This involves the use of site-specific climatological data.

2. Development of Major Input Data

In order to apply the GASPROB code to a consequence assessment of the Bruce HWP, a number of input data sets were required. The major inputs were the topographic and population data for the study area around the Bruce HWP site, the climatology of the site and the release rates of H2S or SO2 for the initiating events postulated in the consequence assessments.

Topographic and population data within a radius of 65 Km of the Bruce HWP were gathered and assembled as a permanent computer file compatible with the code. The file contains the latest population statistics by enumeration areas, the co-ordinates of these areas and their terrain elevations.

The necessary long-term climatological data were not directly available for the Bruce site. However, a data set, in the required form of annual joint frequencies of wind speed, wind direction and atmospheric stability class, was synthesized from data collected over a ten year period at Wiarton, about 56km northeast of the Bruce site. These data were adjusted so as to be more representative of the Bruce site by establishing relationships between simultaneous observations at Wiarton and Bruce for a one year period.

Gas discharge rates for pipe breaks and manway failures were calculated as functions of time for input to GASPROB. The calculations were repeated for a wide range of effective break sizes and possible operator actions, i.e., isolation of the affected process tower or dumping of the tower contents to a flare stack. The discharge of H2S to the atmosphere as a result of a storage tank or tank car failure was treated as a single instantaneous release containing the full tank inventory of H2S mixed with entrained air; in these cases, initial gas densities (heavier-than-air) and temperatures were calculated.

Details of other input data and assumptions used are given in Ref. 3.

3. Initial Sensitivity Analysis

Initially, sensitivity testing of the GASPROB code was carried out to examine the effects on the predicted consequences due to changes in the more uncertain input parameters and assumptions used in the model. This provided estimates of "error bands" on the results of consequence assessments. An additional purpose of this exercise was to determine which model options could be dropped in further runs of the code, thus optimizing computational effort.

The testing was carried out in two stages. First, a number of variables were examined in terms of their effects on the maximum ground level concentrations of H2S predicted by GASPROB. This resulted in the identification of three variables to which the model showed relatively high sensitivity. These, together with several other parameters, were then tested using the full probabilistic consequence model to determine the effect of parameter variations on the distribution of consequences.

4. Full Consequence Assessments

A wide range of initiating events was specified for the programme of full consequence assessments in order to explore the bounds of the possible outcomes. For this purpose, initiating events involving a release of H2S in vapour form were classified according to the size of the break in the pressure envelope, the height of release (low or high), whether or not the release ignites and burns to SO2, whether or not the affected process tower is successfully isolated and, for smaller breaks, whether or not the tower contents are dumped to a flare stack and then successfully ignited or released from the stack as H2S. In the case of smaller breaks, tower isolation was always assumed, but the speed with which this is achieved (slowly or quickly) was included as a variable. Four break sizes were selected, ranging from a single-ended 1300mm diameter break through a 600mm manway failure (single-ended) and a 150mm guillotine (double-ended) break, down to a 50mm guillotine (double-ended) break. Thus, the number of possible combinations of the above factors was 16 for the large breaks (1300mm and 600mm diameters) and 48 for the small breaks (150mm and 50mm diameters).

Due to the considerable cost of running GASPROB for each consequence assessment, statistical experimental design was used to reduce the number of initiating events actually simulated to 40, while showing the major effects of varying each of the above-noted factors, and the major interactions between factors.

The design selected called for all 16 of the large break cases and 24 of the 48 small break cases to be run. A further three cases were also specified: catastrophic failure of a 180 tonne liquid H2S storage tank, catastrophic failure of a 41 tonne tank car of liquid H2S, and failure of a 50mm line carrying liquid H2S.

5. Sensitivity Study of SO2 Toxicity

A single initiating event was chosen for this study involving an SO2 release which, in previous simulations, resulted in the highest expected number of fatalities, i.e., a single-ended 1300mm diameter break at low elevation with no isolation of the affected process tower. This selection was made in order to explore the potential upper bound of the consequences of a burning release. The consequence assessment for this case was repeated assuming an order of magnitude increase or decrease of the LC50 and LC10 functions, both separately and in combination.

C RESULTS

1. Initial Sensitivity Analysis

The results of the sensitivity analyses suggested that the distribution of consequences, or number of fatalities, predicted by GASPROB is most sensitive to the following two factors:

a) The indoor/outdoor effect and, if the persons exposed are indoors, the air change rate of the building. This test produced by far the greatest variation in results, i.e., the number of fatalities with a given probability varied by up to a factor of 100.

b) The number of sub-divisions of the model grid elements (the enumeration areas) used in the code for calculating ground level gas concentrations and consequences.

There was comparatively little, but nonetheless noticeable, sensitivity to the following:

a) The assumed lethal concentration-exposure time relationships for H2S, i.e., the LC50 and LC10 functions.

b) The climatology data input to GASPROB, and

c) The initial mixing ratio of air to gas assumed case of a catastrophic failure of a liquid H2S storage tank.

2. Full Consequence Assessments

For ease of interpretation of the results of the full consequence assessments, the consequence distributions generated by the GASPROB code were presented in the form of histograms. These show, for each of the 43 initiating events, the probabilities of the following consequences: 0, 1 to 5, 6 to 10, 11 to 50, 51 to 100, 101 to 500, 501 to 1000, 1001 to 5000, 5001 to 10,000 and 10,001 to 50,000 fatalities. Two examples of these are given in Figures 1 and 2, for the largest break size (1300mm) and the smallest break size (50mm), respectively.

A number of features of the consequence histograms were noted (all 43 are given in Ref. 3). First, the most likely outcome of all the initiating events tested is zero fatalities, with probabilities ranging from 71% to 100%. This is the case for even the largest break size and is primarily due to the location of the Bruce HWP on the shoreline of Lake Huron and remote from large centres of population (on many occasions any gas released would simply be blown out over the lake). It should be noted, however, that this result would not necessarily apply at another site.

Secondly, the consequence distributions are either bi-modal or multi-modal, i.e., there are two or more peaks in the probabilities. This is also thought to be a result of the particular distribution of population around the Bruce site. Apart from the largest peak for zero fatalities, in most cases there is a significant peak for 101 - 500 fatalities. For the large break cases and liquid H2S releases the probability of this range of fatalities is between 4% and 10%. For the small break cases, this probability is as high as 9%. There is also a significant third peak for 1001 - 5000

fatalities in many of the large break cases, with probabilities of between 1% and 9%.

In addition to the consequence histograms, a single representative statistic was derived to summarize the results of each simulation. The statistic used was the mean number of fatalities, or the "expected value". These mean values are given in Table 1, which also identifies the major factors of the initiating events, e.g. break size, height of release, etc. The table reveals a clear distinction between scenarios where the release is unburned H2S and where there is burning to SO2. In the former cases, the mean number of fatalities is in the hundreds (117 - 506), while in the latter cases the means are much lower (9 - 81). This is presumably the result of two phenomena; the assumed lower toxicity of SO2 compared to H2S and the rise of gases due to the heat of combustion, thus producing lower concentrations at ground level.

An analysis of variance was conducted on the mean values in order to separate the observed variation in the results into components due to the factors specified in the experimental design, e.g., break size, height of release, etc. This analysis showed that relatively few of the identified factors affected the outcome of the consequence analysis of large size breaks (1500mm and 600mm diameter). The only significant factors were, in order of importance, whether or not the release burns to SO2, the break size and whether or not the affected process tower is successfully isolated. Furthermore, any reasonable change in the criterion for statistical significance would not change this result. By contrast, many more factors contributed to the variance of the results for the small break sizes (150mm and 50mm diameter). The significant factors were the break size, burning of the release and whether or not the process tower contents are dumped to the flare stack. As well, in the small break scenarios, most of the two factor combinations, e.g., break size with release height, were found to have a significant effect on the results. Thus, the consequences of small breaks appear to be much more sensitive to the conditions specified.

3. Sensitivity Study of SO2 Toxicity

This study investigated the sensitivity of the consequences predicted by GASPROB to the assumed lethal concentration-exposure time functions (LC50's and LC10's) for SO2. The results, applicable to the Bruce HWP, showed a distinct sensitivity to both the LC50 and LC10 functions selected, although this was greatest for the LC10 functions. For example, there is a factor of 10 difference in the probabilities of over 1000 fatalities due to changes in the LC10, and a factor of 2 to 3 difference in the probabilities of over 5000 fatalities due to changes in the LC50.

4. Results of Other Studies

In the appendix to this report, a review of the recent literature on H2S toxicity is documented with emphasis on the concentration-exposure time functions of interest in this study. No new data of relevance were identified. However, older data from the 1940's, which were not included in the last review for the AECB (Ref.5), tend to confirm the concentration-exposure time functions used in GASPROB.

A peer review by Ontario Hydro of the scope determination phase of this programme (Ref.1) suggested that the process operating pressure assumed in the derivation of H2S release rates may be overstated by about 11%. In addition, Ontario Hydro has indicated that the liquid H2S storage tanks at the Bruce HWP are never filled to capacity (180 tonnes), which was assumed in the catastrophic failure scenario. Instead, the maximum operating capacity was given as 144 tonnes.

The likely effects of these changes on the consequences predicted by GASPROB have been addressed in an appendix to this report. A minor reduction in some consequence probabilities is expected as a result.

5. Applicability and Limitations of Results

The GASPROB model and the input data used in the consequence assessments were selected on the basis of a "best estimate" philosophy. Furthermore, the sensitivity analyses showed that most of the model options and inputs, if changed within reasonable limits, would have little effect on the results.

However, some significant sensitivites were shown to a few of the parameters, suggesting some limits on the validity of the predicted consequences, as follows:

a) To keep computer run times and costs within reasonable limits, the number of model grid elements used was restricted after the first few kilometers downwind of the HWP. Although fatalities would most frequently occur in the near field of the model and spatial definition is of diminishing importance further downwind from the release point, the grid of elements used in GASPROB may have been a source of some error in the consequence distributions. This error cannot be quantified at present, but it is thought that any such error would be manifested as an underestimate of fatalities.

b) Uncertainties in the lethal dose relationships for both H2S and SO2 are possible sources of error. However, the results of the sensitivity studies of both H2S and SO2 toxicity can be used to indicate "error bands" for the predicted consequences.

c) Some sensitivity to input climatology was noted. As discussed earlier, no site-specific atmospheric stability data were available for the Bruce plant, so data from Wiarton were used to develop a long-term climatology for Bruce. It is thought that the results of the full consequence analyses may be underestimated by a relatively small fraction due to this source of error. In addition, the lakebreeze effect was not included in the full consequence runs. The sensitivity analyses indicated a significant increase in the predicted probabilities if the effect were included, although the lakebreeze model used in the sensitivity tests is believed to have overstated this increase.

Finally, it must be emphasized that the results of the sensitivity analyses, the full consequence assessments and the above statements concerning the accuracy of the predicted consequences are specific to the Bruce heavy water plant. Considerable variations can be expected if the same exercise were applied to another site.

D. CONCLUSIONS AND RECOMMENDATIONS

1. Summary of Major Conclusions

A number of important conclusions can be drawn from the results of the full consequence assessments

carried out for the Bruce heavy water plant. They are summarized below:

a) The most likely outcome of an accidental release of H2S is zero fatalities. This result is very much a function of the particular population distribution around Bruce, and would not necessarily be repeated at another heavy water plant site.

b) The consequence distributions are bi-modal or multi-modal with, in most cases, a significant peak probability in the 101 - 500 fatalities range.

c) In the large break scenarios (600 and 1300 mm diameter),burning of the H2S release would reduce the expected number of fatalities by about a factor of 10. The effect of burning in the small break cases (150 and 50 mm diameter) is generally weaker than in the large break cases, but is still noticeable.

d) For scenarios involving large breaks (600 and 1300 mm diameter), the effects of burning of the release, break size and tower isolation are significant.

e) For scenarios involving small breaks, the significant factors are break size, burning of the release, dumping to flare and most two-factor combinations. The speed with which a process tower is isolated is not significant.

f) Relatively few of the identified factors affected the outcome of the consequence analysis of large break sizes. On the other hand, many more factors contributed to the results for the small break sizes. Thus, the consequences of the small breaks appear to be much more sensitive to the conditions of release.

Finally, in the addendum to this report, it is concluded that there are no recent studies on H2S toxicity which review the concentration-exposure time function of interest in this study. Older data from the 1940's, which were not included in the last review for the AECB (Ref.5), tend to confirm the functions used in GASPROB.

2. Summary of Recommendations

In view of the results of the sensitivity analyses identified earlier in this report, recommendations for

further studies were made in some areas which might reduce the uncertainties associated with the GASPROB predictions. These were:

a) A further review of the relevant experimental evidence on the initial mixture of H2S and air which would result from the catastrophic failure of a liquid H2S storage tank or tank car. If necessary, specific experiments on H2S under field conditions might be considered.

b) An update of the dispersion climatology of the Bruce site once a more complete data set has been accumulated from ongoing measurements at the site.

c) A limited number of additional sensitivity tests of GASPROB to investigate the effects of increasing the number of model grid elements on some of the results obtained in this study.

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TABLE 1

MEAN NUMBER OF FATALITIES FROM
FULL CONSEQUENCE RUNS

RUN NO.	BREAK SIZE	ISOLATION	HEIGHT	BURN AT BREAK	DUMP TO FLARE	IGNITION AT FLARE	MEAN NUMBER OF FATALITIES
1	600	NO	LOW	NO			413
2	1300	NO	LOW	NO			516
3	600	YES	LOW	NO			311
4	600	NO	HIGH	NO			354
5	600	NO	LOW	YES			51
6	1300	YES	LOW	NO			484
7	1300	NO	HIGH	NO			502
8	1300	NO	LOW	YES			81
9	600	YES	HIGH	NO			270
10	600	YES	LOW	YES			48
11	600	NO	HIGH	YES			51
12	1300	YES	HIGH	NO			481
13	1300	YES	LOW	YES			69
14	1300	NO	HIGH	YES			81
15	600	YES	HIGH	YES			48
16	1300	YES	HIGH	YES			69
17	50	FAST	LOW	NO	NO		26
18	150	SLOW	LOW	NO	NO		159
19	150	FAST	HIGH	NO	NO		117
20	150	FAST	LOW	YES	NO		9
21	50	SLOW	HIGH	YES	NO		15
22	50	SLOW	LOW	NO	NO		0
23	50	FAST	HIGH	YES	NO		0
24	150	SLOW	HIGH	YES	NO		10
25	150	FAST	LOW	YES	YES	NO	179
26	50	SLOW	LOW	NO	YES	NO	47
27	50	FAST	HIGH	NO	YES	NO	25
28	50	FAST	LOW	NO	YES	NO	18
29	50	FAST	LOW	YES	YES	YES	26
30	150	SLOW	HIGH	NO	YES	NO	130
31	150	SLOW	LOW	YES	YES	NO	15
32	150	SLOW	LOW	NO	YES	YES	159
33	150	FAST	HIGH	YES	YES	NO	15
34	150	FAST	HIGH	NO	YES	YES	117
35	150	FAST	LOW	YES	YES	YES	14
36	50	SLOW	HIGH	YES	YES	NO	18
37	50	SLOW	HIGH	NO	YES	YES	15
38	50	SLOW	LOW	YES	YES	YES	5
39	50	FAST	HIGH	YES	YES	YES	5
40	150	SLOW	HIGH	YES	YES	YES	12
41							304
42							55
43							158

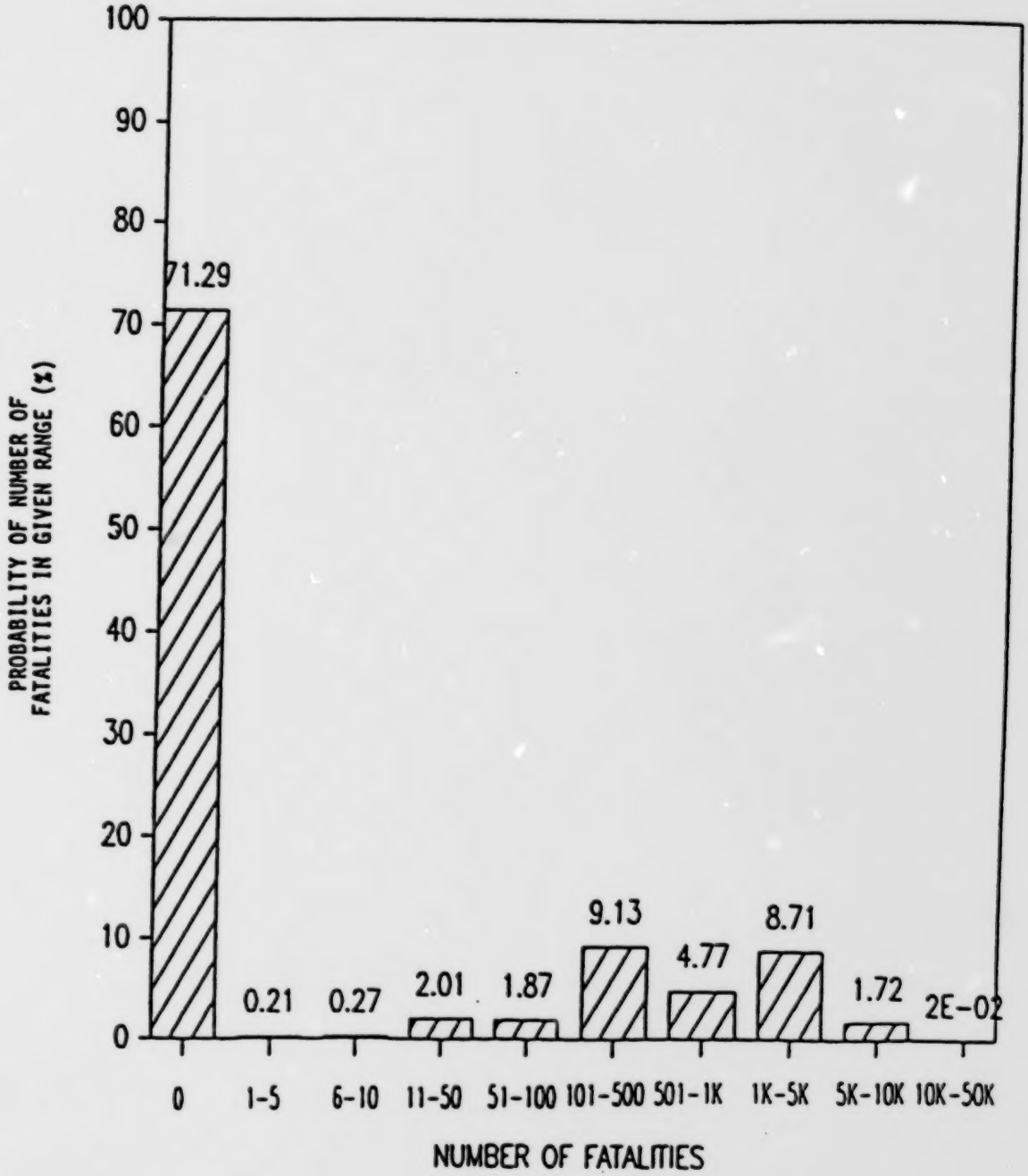

FIGURE 1

CONSEQUENCE HISTOGRAM FOR SINGLE-ENDED 1300 MM DIAMETER BREAK IN PRESSURE ENVELOPE (RUN NO. 2 IN TABLE 1, I.E., ASSUMES NO PROCESS TOWER ISOLATION, RELEASE AT 10M ABOVE GROUND AND BURNING OF H_2S TO SO_2.)

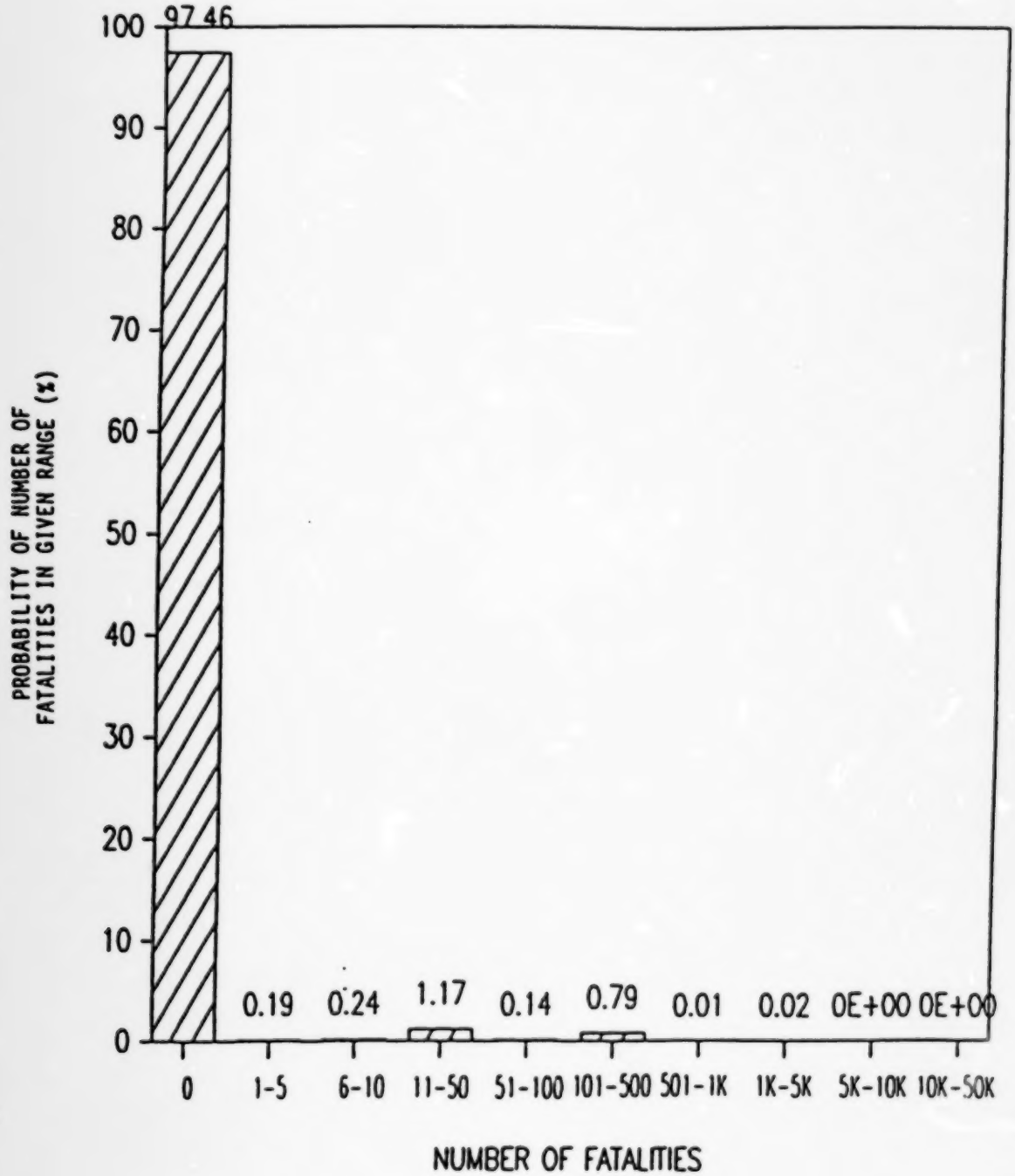

FIGURE 2

CONSEQUENCE HISTOGRAM FOR GUILLOTINE 50MM DIAMETER BREAK IN PRESSURE ENVELOPE
(RUN NO. 39 IN TABLE 1, I.E., ASSUMES FAST PROCESS TOWER ISOLATION, RELEASE AT 80M ABOVE GROUND AND BURNING OF H_2S TO SO_2.)

APPENDIX A

THE ACUTE TOXICITY OF HYDROGEN SULFIDE

- AN UPDATE OF THE LITERATURE

BY

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THE ACUTE TOXICITY OF HYDROGEN SULFIDE - AN UPDATE OF THE LITERATURE

1. INTRODUCTION

In 1981, the Atomic Energy Control Board of Canada (AECB) commissioned Monserco Limited, of Mississauga Ontario, to conduct an extensive review of the toxicity of hydrogen sulfide (H_2S) with emphasis on acute and sub-acute poisoning (A1). The review used data from animal studies and human exposures to derive a lethal dose relationship appropriate for the general population. In addition, a statistical model was developed to calculate the probability of short-term concentration peaks on exposure risks in the vicinity of an atmospheric release of H_2S.

In 1985, Monserco Limited again undertook to review the literature on H_2S on behalf of the AECB. The purpose of this second review was to examine the literature which has been published in the last five years, evaluate its pertinence and relevance to acute and sub-acute human toxicity, and to see if any new data would either modify or substantiate the conclusions of the original 1981 report.

In order to ensure that no pertinent reports were missed, the major medical, scientific, and toxicological data bases were accessed and searched for all entries containing 'hydrogen sulfide' or its Chemical Abstracts Service (CAS) number, in either the article title or its abstract. The data bases searched included the Registry of Toxic Effects of Chemical Substances (RTECS), the Toxicology Data Bank (TDB), Embase (from Excerpta Medica), Toxline and Medline (both from the U.S. National Library of Medicine).

As an added check, to ensure that all literature had been covered in the original 1981 report, a limited search was carried out for pre-1979 data in Toxline.

These data base searches produced over 200 citations relating to H_2S toxicity, and all of these abstracts were reviewed. Papers which related to acute toxicity in animal studies, or acute exposure poisonings in human accident situations, were ordered through library facilities. Each of these published studies was appraised.

2. ANIMAL STUDIES

In the period 1979 to 1985, only one new study relating to the acute toxicity of H_2S could be located (A2). In this particular study, H_2S was not the main chemical under investigation, but rather methyl mercaptan, since this gas together with H_2S, dimethyl sulfide, and dimethyl disulfide constitute the major components of reduced sulfur gases emitted from kraft pulp mills in the paper industry. Dose response relationships for methyl mercaptan were obtained in detail, but only a 4-hour LC_{50} value of 444 ppm for H_2S was reported. No further data are given for exposures during shorter time periods, and this publication does not fall within the 100-minute exposure time period, which was the focus of study in the 1981 Monserco report.

Although no new acute animal toxicity data impacting upon the 1981 Monserco report was published in the time period 1979 to 1985, the computer literature search of pre-1979 reports discovered two pertinent articles in a poorly known, but reputable, journal (A3,A4). These reports made extensive studies of H_2S and are remarkable for their detailed

investigations using rats, mice, and house flies. The data derived from these investigations falls within the definition of the original Monserco study.

The studies by Weedon et al (A3) on the house flies were discounted for the purposes of this review. However, the LC_{50} derivations made by these authors from their rat and mouse studies were obtained from their lethal dose versus time plots that are reproduced in Figures A1A-C. These points were then added to the plot of the 1981 Monserco study, as shown in Figure A2. Both the LC_{50} for the mouse and rat studies fall within the scatter plot range of data obtained from the works of other authors (A5,A6,A7).

3. CASES OF HUMAN EXPOSURE

The most up-to-date statistics on H_2S exposures are those published by Arnold et al (A8) who reported a five-year retrospective study of workers exposed to hydrogen sulfide in Alberta. Out of 250 cases, 78.4% resulted in up to two days of lost time. Details are reproduced in Table A1.

Despite the well known effects of H_2S, and the dangers associated with overexposure in several well defined occupations, instances of accidental death and severe poisoning continue to be regularly reported in the literature. In the period 1979 to 1985, 13 such reports were located. The appropriate publications were obtained and reviewed. A summary of the findings is presented in Table A2.

A striking feature of the most recent reports on human accidental exposure to H_2S is that the majority relate to farming operations although reports of accidents associated

with industrial processes still appear frequently. In many of the farm accident reports, manure and sewage pits located under barns containing cattle and pigs were entered for maintenance and repair. Usually, the first worker entering was overcome and was then followed by others who tragically met with the same fate. In some instances, five or six people would die in vain attempts to rescue fellow workers or family members. Usually, no follow-up measurements were carried out, and in those instances where a subsequent investigation was conducted, H_2S measurements are simply recorded as "off-scale" (implying greater than 600 ppm).

In addition, interpretations of the toxicity of H_2S in these farm accidents is confounded by the high levels of methane, a simple asphyxiant and carbon monoxide which are also present in the manure pits. In one instance, over 4,000 ppm of methane and over 100 ppm of carbon monoxide were recorded along with off-scale measurements of H_2S. For this review, none of the farm accidents and fatalities attributed to H_2S exposure could be used to question or substantiate existing parameters.

For the purposes of this study, the most useful accidental poisoning report was made by Vannatta (A9). In this accident, four workers entered a sludge tank to carry out routine clean-up operations. The tank had previously been well flushed with fresh air and H_2S levels had been measured prior to entry of personnel. The levels were found to be well within safe limits. The cleaning process involved using an acidic solution to remove sludge from the walls of the tank. After four men had been working in the tank for about 15 minutes, one of them remarked on a peculiar taste in his mouth and suggested to the others that they all leave the tank. One worker made it to the door, but collapsed just outside, the others collapsed inside the tank. Fortunately, company safety procedures had been followed

and a fifth worker who had been stationed outside the tank sounded the alarm, put on an air-supplied respirator and was able to rescue the remaining three workers inside the tank. All recovered rapidly and suffered no long-term disabilities.

Subsequent investigation by the plant occupational hygiene personnel showed that the acid cleaning solution had reacted with sulfur compounds in the tank sludge to produce H_2S. A careful reconstruction of the incident showed that the workers had been exposed to around 200 ppm for 15 minutes. The reconstruction was achieved by four personnel, wearing air-supplied respirators, re-entering the tank and begining clean up operations in the same way as the four original workers. Air monitoring for this was carried out during the clean up process.

A further report by Klausen et al (A10) describes an instance in which a sewer worker first showed signs of dementia before collapsing when exposed to a pocket of H_2S in a sewer. Follow-up measurements indicated an exposure of 200 ppm for 10 to 15 minutes.

The exposure levels leading to unconsciousness, as recorded in these two reports, correlate relatively well with previous data noted in the 1981 Monserco report and attributed to Ahlborg (A11). A further study also referred to in the original Monserco study (A12), reported unconsciousness at a level of 1,000 ppm for approximately 20 minutes. This accident was a near fatality and the 1,000 ppm level for the indicated time period is probably much higher than that which can induce unconsciousness at its lowest threshold. The data provided by Klausen et al (A10) and Vannatta (A9) suggest that a level of 200 ppm for 10 to 15 minutes is adequate to cause unconsciousness. The points from this new data are shown in Figure A3, which is taken from the 1981 Monserco report.

4. MECHANISM OF TOXICITY

In the last five years, the most significant research on the acute toxicity of H_2S has centred on the biochemical mechanism of its toxicity. This may, in part, be due to controversy that has developed in this area. Early reports on the mechanism of H_2S toxicity all remarked on the apparent similarity between the mode of action of H_2S and that of hydrogen cyanide (HCN) (A6,A13,A14). These early comparisons were apparently based on the speed with which H_2S could cause respiratory paralysis. The time interval for respiratory arrest is very similar to that caused by HCN poisoning.

The authors of these earlier publications tended to discuss the mechanism of toxicity in physiological ratner than biochemical terms. Mitchell and Yant (A6), for example, referred to two lethal modes of action for H_2S toxicity. Firstly, they identified an acute poisoning which involved respiratory failure followed by cardiac arrest and a subacute type involving irritation of the respiratory tract and pulmonary edema. Haggard (A13) described a similar system when he reported that H_2S could act as an irritant where its effects could range from minor irritation of the mucus membranes to edema of the lungs. He also described systemic poisoning, in which nerve system toxicity leads to respiratory failure.

As biochemical mechanisms in human metabolism were elucidated during the last 60 years, interest has grown in the metabolism and toxicity of H_2S at the biochemical level. The current state of knowledge on the biochemical pathways of H_2S was recently presented in a review by Beauchamp *et al* (A15) and is reproduced in Figure A4. Figure A4 shows that toxicity occurs with the enzyme cytochrome oxidase. This enzyme is the last one in the biochemical sequence known as the respiratory chain,

and represents the final step in the reduction of oxygen for the production of energy. Studies at the cellular level (A16) have demonstrated that sulfide will block activity at the cytochrome oxidase enzyme. This mode of action appears exactly analagous to that of cyanide which also exerts its influence upon cytochrome oxidase.

This analogy with cyanide has been taken even further in the literature. So much so, that antidote therapies used in the treatment of HCN poisoning (e.g. sodium nitrite therapy) are now widely advocated in literature from the United States as effective for the treatment of H_2S poisoning (A17,A18,A19). The rationale for this treatment is shown in Figure A5.

Interestingly, the enthusiasm for the nitrite-based therapy and the analogy between H_2S and HCN poisoning that comes from the United States is not shared by Canadian researchers in this field and has lead to some heated exchanges on this topic (A20).

Basic researchers, both in the United States (A21) and elsewhere (A22), have assumed in their experimental studies that the toxicity of H_2S upon the nervous system is primarily related to the inhibition of cytochrome oxidase within nerve tissue. This assumption is contested by a group of researchers in this country (A23). These authors have studied nerve impulse conduction in the axons of a species of frogs, and claim that in nerve tissue, at least, the mode of action of H_2S and HCN are not comparable.

To support their viewpoint, they cite the work of Nicholls and Kim (A16) who demonstrated that more than one sulfide per cytochrome oxidase unit was needed to block the respiratory function of the oxidase, and that detoxification of this step

was extremely rapid. This is quite distinct from the cyanide cytochrome oxidase combination which requires only one cyanide and is much more stable and long-lasting.

Their research indicates that H_2S may exert its action in a manner more akin to a simple, short acting anesthetic or an organophosphate pesticide than to HCN. They have been able to demonstrate that the HS- ion, which is present during H_2S poisoning, can combine with Ca^{2+} in nerve tissue preparations. Ca^{2+} is essential for nerve impulse transmission. They have also demonstrated that sulfide ion can interfere with the acetylcholine receptors, which are present in certain nerve endings. This group of authors strongly questions the efficacy and usefulness of nitrite treatment, and has stated that it is contraindicated (A23) in H_2S poisoning. This viewpoint is also supported in reference A24.

The controversy surrounding the metabolic basis of H_2S toxicity will almost certainly ensure continued interest and regular publication on this topic by the various parties involved.

5. CONCLUSIONS

Over the last five years there have been no further studies on animal models which review the dose-response relationship with hydrogen sulfide exposure. Older data from the 1940's, which was not a part of the last Monserco review, tend to confirm and substantiate the parameters delineated in the 1981 Monserco report.

Serious overexposures and accidents leading to death resulting from hydrogen sulfide, continue to be reported on a regular basis. Two of these reports indicated unconsciousness at

200 ppm for between 10 and 15 minutes. Data from these two reports can be superimposed on Figure A2 of the 1981 Monserco report and do not substantially alter the parameters determined though they perhaps suggest a more conservative estimate of the levels producing unconsciousness.

By comparison with some other industrial gases, the dose-response relationship for human exposure to hydrogen sulfide seems to be remarkably well documented. Although there are some variations in dose and response relationships, delineated by different authors, by and large there is a general agreement about the effects that occur within certain concentration ranges.

In the last five years, substantially more data has been published which relates to the mechanism of toxicity of H_2S at the biochemical level. It is anticipated that over the next few years, this area will form the focus of interest for most research groups working the area of H_2S toxicity.

This review, and an extensive review conducted by Beauchamp et al (A15), indicates that there have been no substantial new additions to the literature that would merit a re-evaluation of the parameters delineated in the 1981 Monserco report. Such new data that has come to light tends to substantiate the existing derivations.

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TABLE A1 - DISTRIBUTION OF LOST TIME

LENGTH OF TIME LOST, DAYS	FREQUENCY	PERCENTAGE
0-2	196	78.4
3-5	19	7.6
6-14	15	6.0
Greater than 14*	20	8.0
Total	250	100.0

* Seven cases were fatal.

From Arnold et al (A8). 78.4% of exposures resulted in two days or less of lost time. Compensation costs in 73.6% of cases were associated with hospital or medical fees and amounted to around $75 per case. Compensation awards of less than $2,000 occurred in 58 cases (28.2%) and were associated with lost time from work (usually less than a month).

TABLE A2 - SUMMARY OF OCCUPATIONAL H_2S POISONINGS - 1978-1985

	LANGUAGE	INDUSTRY	RESULT	# CASES	EXPOSURE
Klausen et al (A10)	Danish	sewer-works	- unconsciousness	1	200 ppm for 5-10 min
Seuren (A25)	Dutch	farming	- dizziness, near collapse	ND	ND
Heimdal (A26)	Norwegian	farming	- unconsciousness	1	ND
Hoyem-Johansen (A27)	Norwegian	?	- lung edema	2	50-100 ppm for 30-60 min (estimate)
Morse et al (A28)	English	farming	- unconsciousness	1	60 ppm for 10 min
			- death	1	ND
Osbern & Crapo (A29)	English	farming	- unconsciousness	1	ND 2-3 min
			- lung edema	1	
			- death	3	
Peters (A30)	English	hospital	- unconsciousness	1	1000 ppm for 2-3 min (estimate)
Donham et al (A31)	English	farming	- death	5	ND
			- dizziness, near collapse	2	ND
			- unconsciousness	1	ND
			- death	3	400 ppm (time unknown)
James (A32)	English	sewer-works	- death	3	600 ppm (time unknown)
Komura et al (A33)	Japanese	?	- death	5	ND
Vannatta (A9)	English	oil refinery	- unconsciousness	4	200 ppm for 15 min (estimate)
Celesti & Ferretti (A34)	Italian	industrial	- death	4	ND
Hagley & South (A35)	English	farming			150 ppm (time unknown)

ND = no data

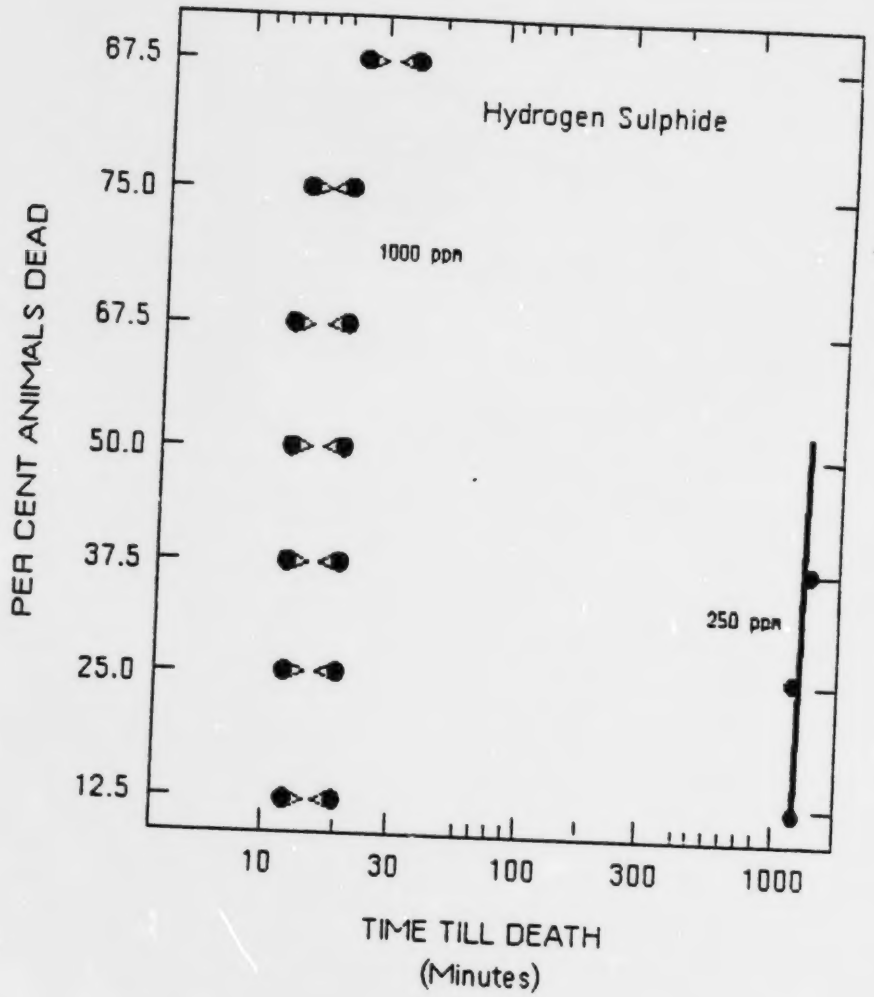


FIGURE A1.A – TIME MORTALITY CURVE FOR RATS EXPOSED TO H_2S
From Weedon et al (A3)

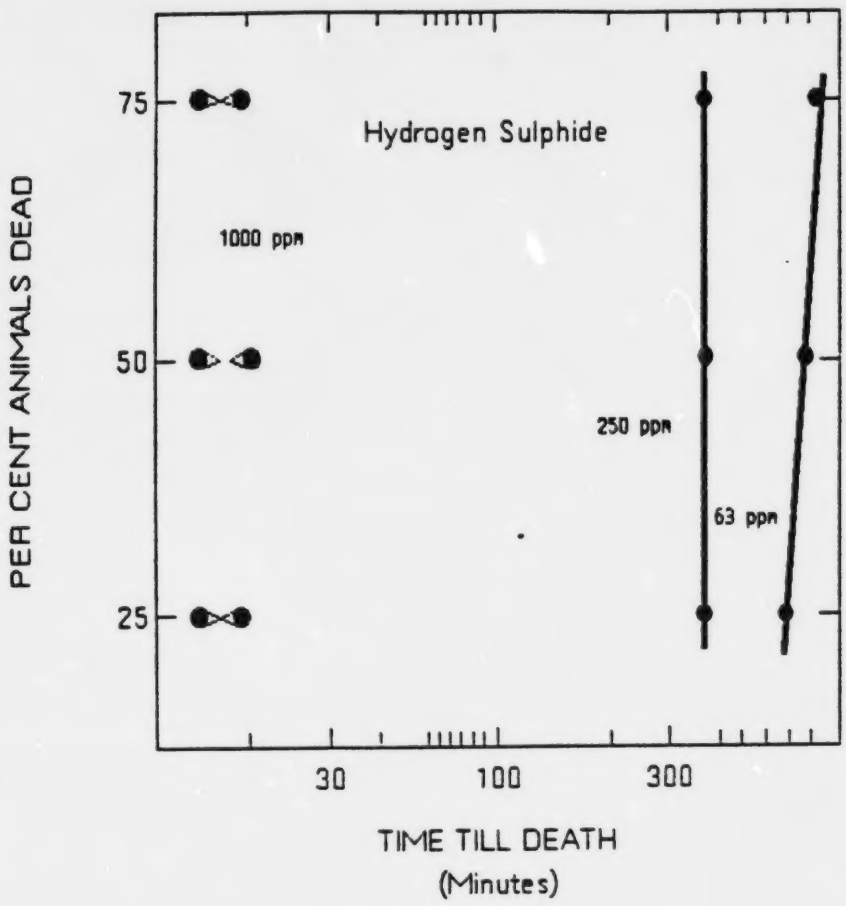


FIGURE A1.8 – TIME MORTALITY CURVE FOR MICE EXPOSED TO H_2S
From Weedon et al (A3)

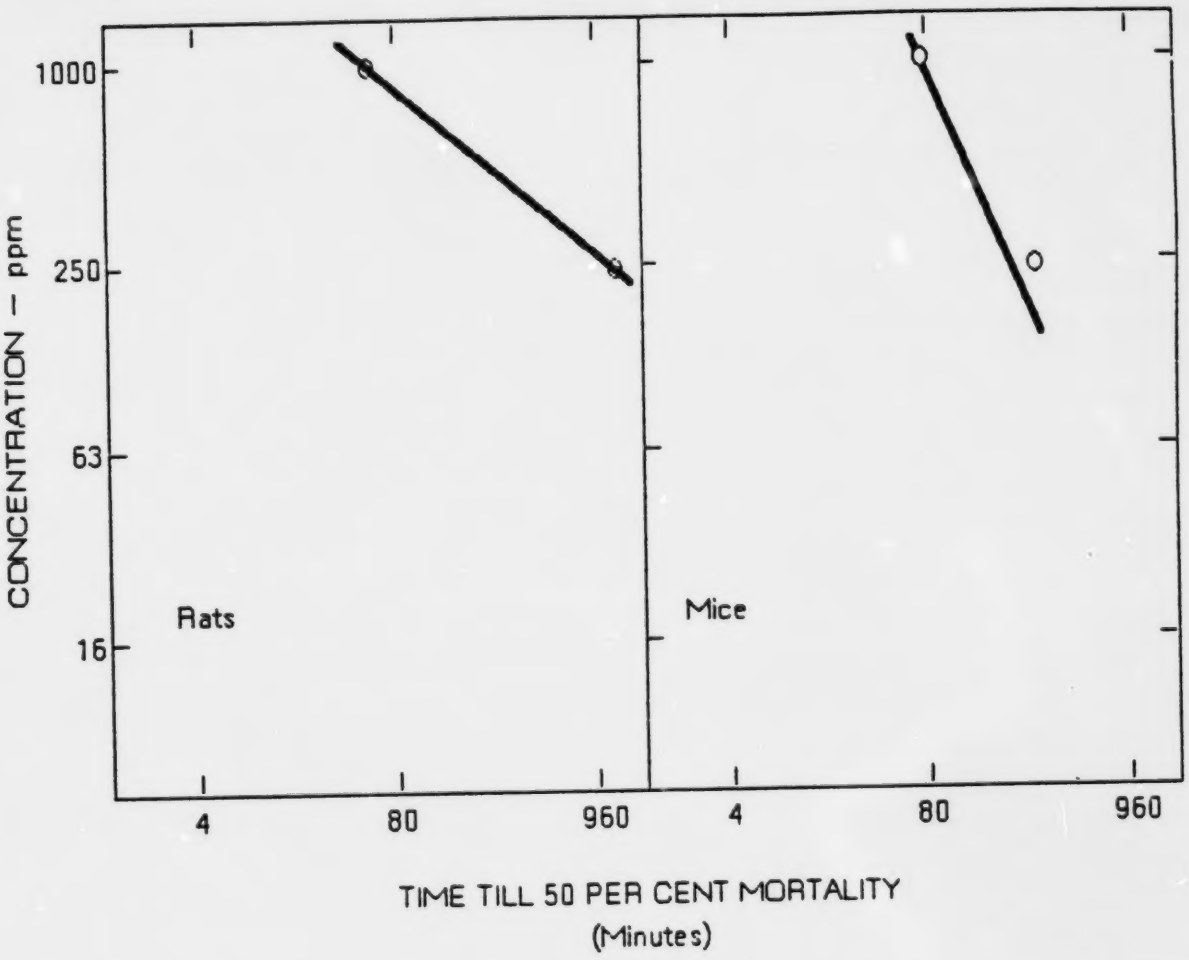
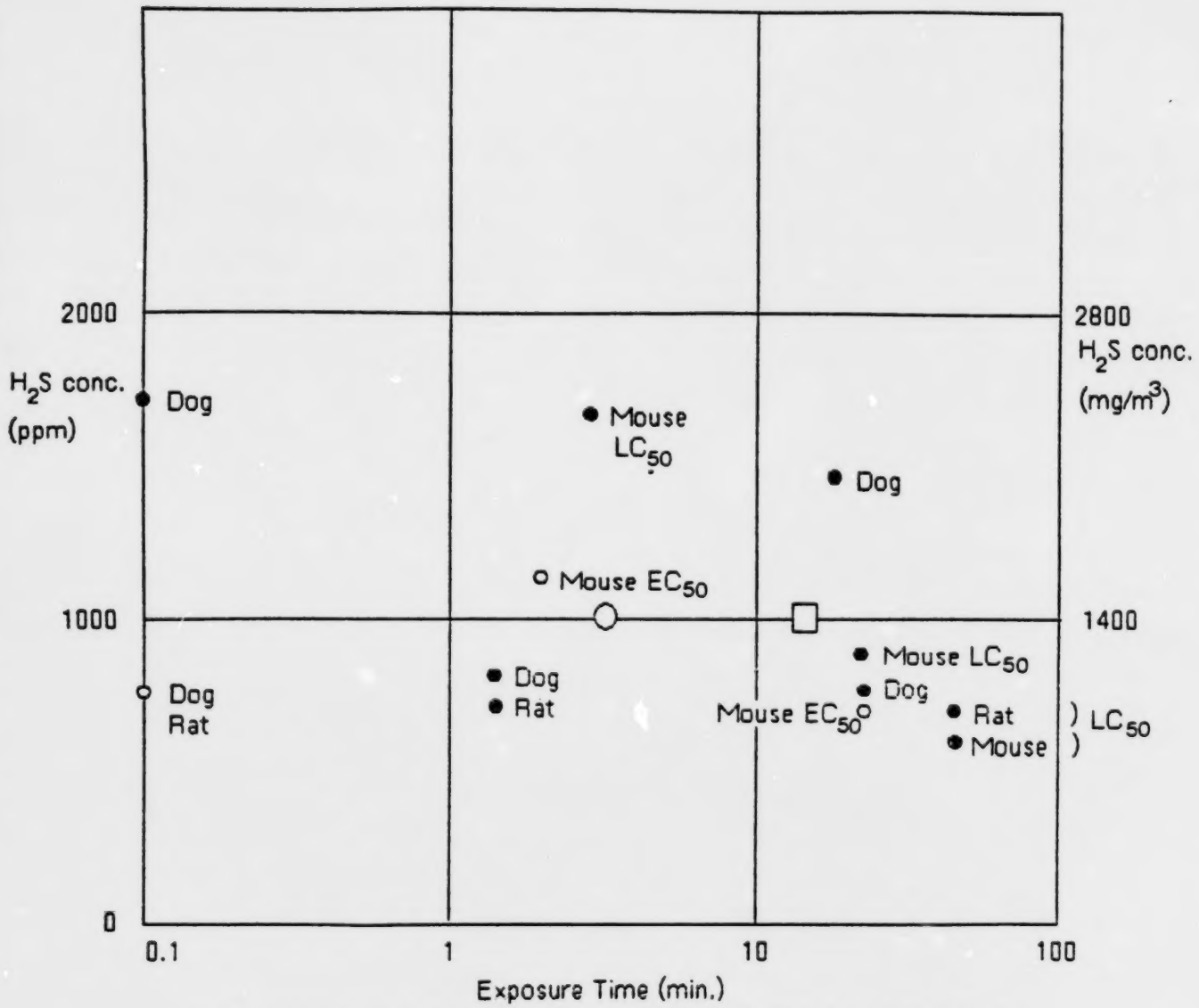


FIGURE A1.C – TIME CONCENTRATION CURVES AT 50% MORTALITY FOR RATS AND MICE EXPOSED TO H_2S
From Weedon et al (A3)



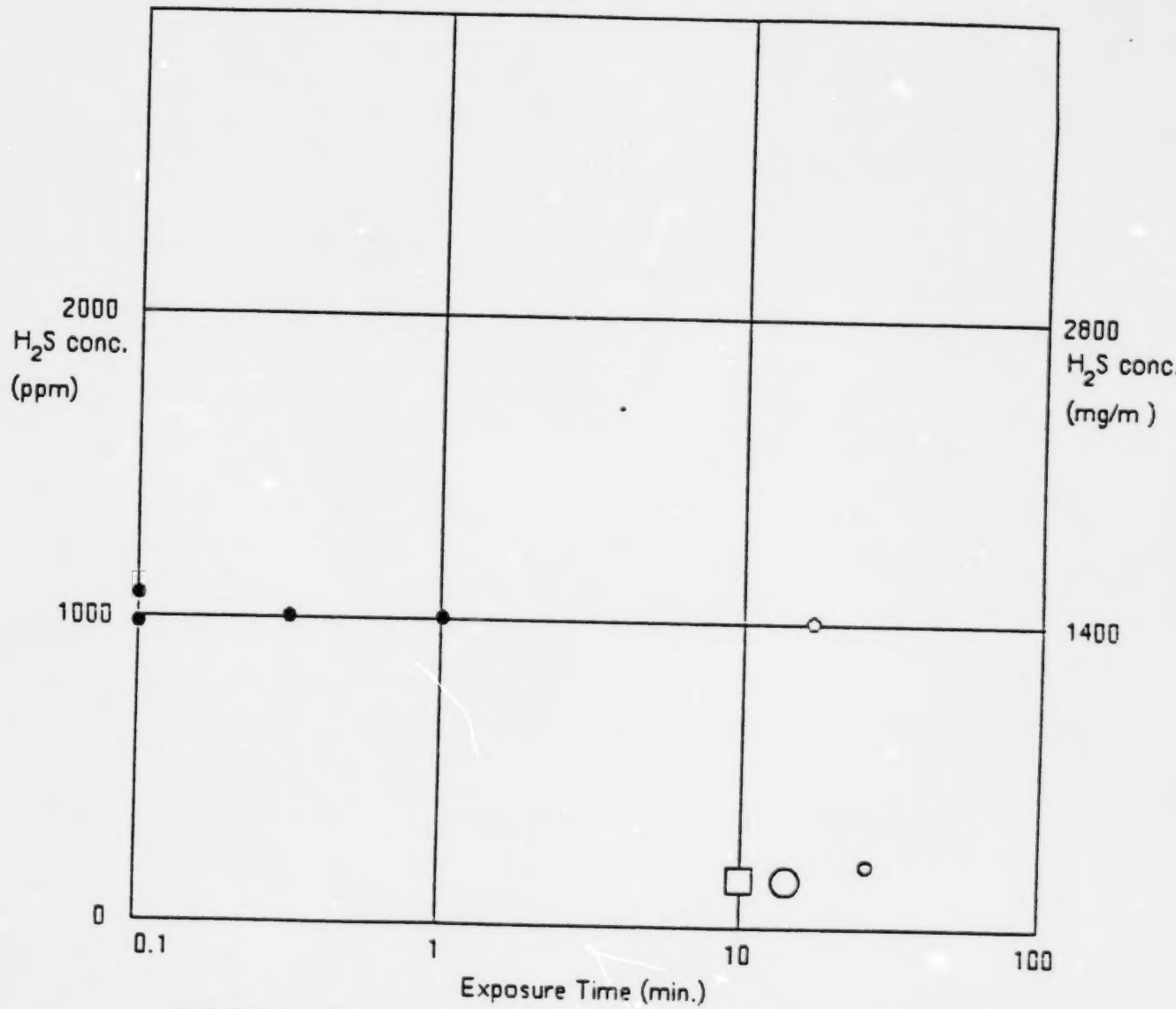
H_2S DOSES FOR LETHALITY OR UNCONSCIOUSNESS IN ANIMALS

FIGURE A2 – DATA FROM WEEDON ET AL (A3) FOR MICE ○ AND RATS □ ADDED TO DATA PLOT FROM MONSERCO REPORT (A1)

Key

- ● Lethality
- ○ Unconsciousness

LC_{50} (lethal concentration 50%) is the concentration of a chemical which will kill 50% of the test animals. The EC_{50} (Effective concentration 50%) is that concentration of a chemical which will produce a specified effect in 50% of the test animals. In this instance the effect noted was the inability of mice to 'right' themselves once turned on their backs. This represents the earliest stage of unconsciousness.



H_2S DOSES FOR LETHALITY OR UNCONSCIOUSNESS IN HUMANS

FIGURE A3 – DATA FROM KLAUSEN ET AL A10 □ AND

VANNATTA ○ ADDED TO PLOT FROM MONSERCO REPORT(A1)

Key

- ● Lethality
- ○ Unconsciousness

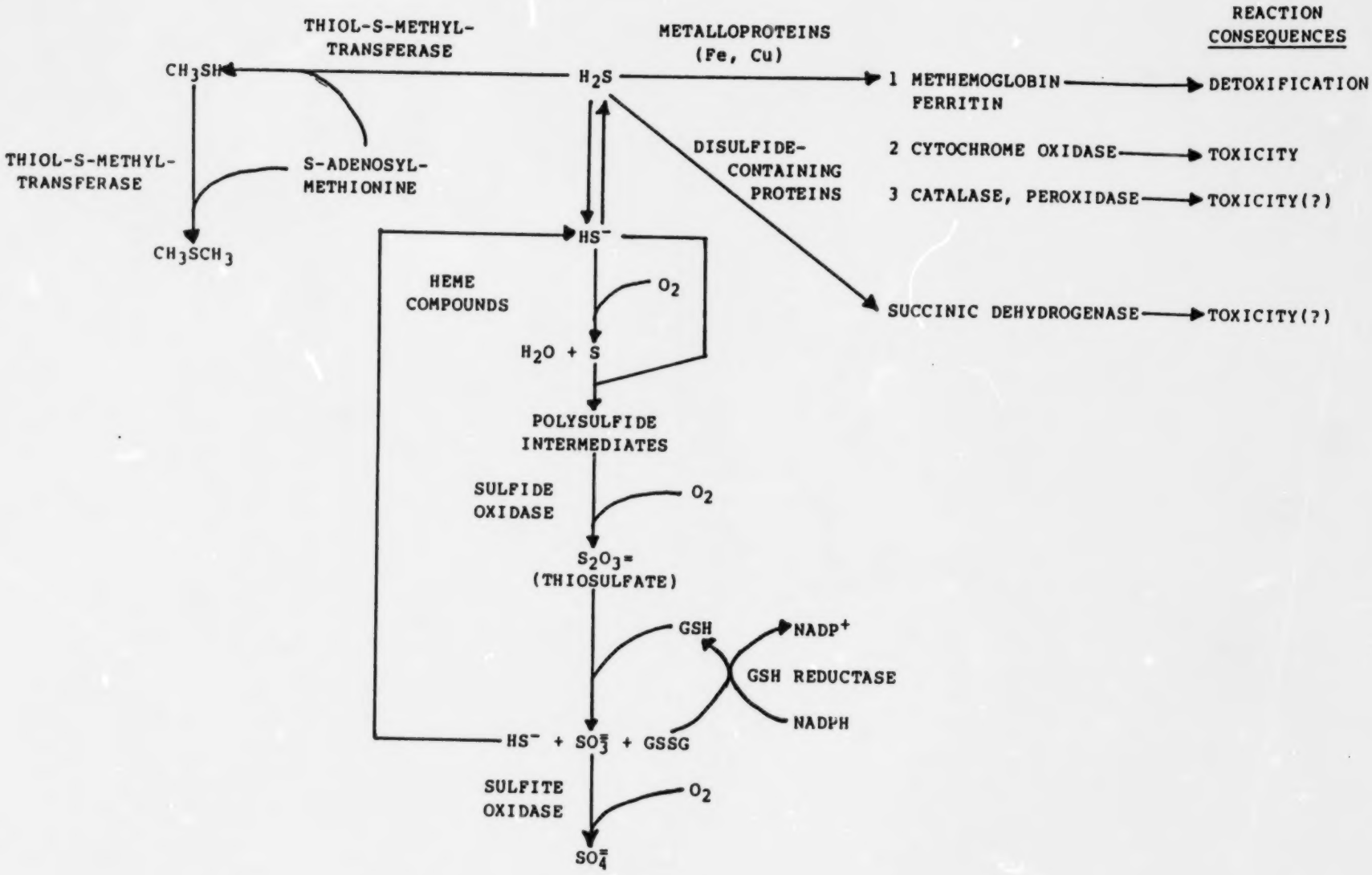


FIGURE A4 - METABOLISM OF H_2S
From Beauchamp (A15)

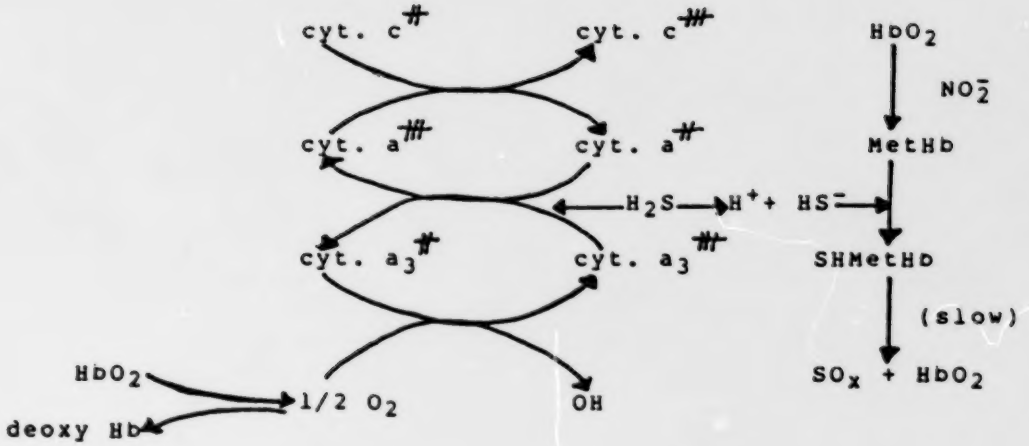


FIGURE A5 - PRINCIPLES OF SULFIDE POISONING AND ITS THERAPEUTIC MANAGEMENT
From Smith and Gosselin (A18)

Undissociated hydrogen sulfide inhibits the function of cytochrome oxidase (aa_3) by an unknown mechanism. Since it is the terminal enzyme in the electron transport chain, molecular oxygen cannot be reduced, and oxygen utilization decreases. Oxidative metabolism may slow to the point where it cannot meet metabolic demands. In the central nervous system this lesion may result in death by respiratory arrest. On the injection of an appropriate dose of sodium nitrite, a tolerable concentration of methemoglobin is generated which can complex with the hydrosulfide anion to form sulfmethemoglobin. The latter decays spontaneously with a half-life of about two hours to form oxyhemoglobin and an unknown oxidized form of sulfur.

APPENDIX B

REVISIONS TO AECB RESEARCH REPORT INFO-102-1:

Probabilistic Consequence Assessment of Hydrogen Sulphide Releases from a Heavy Water Plant: Scope Determination

(revisions are underlined)

1. Introduction

Heavy water (deuterium oxide) is an essential material in the Canadian nuclear industry, since it acts as both moderator and coolant in the present generation of CANDU reactors. Although heavy water occurs naturally in water bodies, the required quantities and purity for reactor use must be obtained by separating the heavy water from the light water with which it is diluted, normally in the ratio of about 6500 to 1. In Canada, this process is carried out in heavy water plants employing the Girdler-Sulphide method. There are three such plants currently in operation at Glace Bay and Port Hawkesbury, Nova Scotia, and Bruce County, Ontario. The plants are of considerable scale and complexity and, in general appearance and mode of operation, not unlike many other petro-chemical installations found across the country. In common with such installations, heavy water plants also require the use of toxic chemicals. In particular, the Girdler-Sulphide process employs large quantities of hydrogen sulphide (H_2S) which is recognized as a potential source of hazard to both the workforce and the general public in the vicinity of the plants. Although extensive precautions and contingency plans are in place to minimize the risk of exposure to injurious levels of H_2S, further study of this question is important to both operators and regulators as they seek to further reduce this risk.

This report is concerned with the evaluation of the consequences of an accidental release of H_2S gas to the atmosphere following a pipe or pressure envelope failure, or some other process upset, at a heavy water plant. It is also concerned with the emissions of sulphur

to the receptor is then primarily weather and terrain dependent and results in a certain pattern of gas concentrations downwind. The number of casualties, or receptor response, is determined as a probability distribution.

3. Initiating Events

3.1 Potential Sources of Release

3.1.1 Process Description

At Canadian heavy water plants the extraction of heavy water is carried out by the Girdler-Sulphide process. The initial stage of extraction is performed in Enriching Units, which provide a product stream containing about 25 mol percent of deuterium to the Finishing Units. The latter units then further concentrate the product to the required purity of 99.75 mol percent. Hydrogen sulphide is used in the Enriching Units, each unit having an H_2S inventory of some 540 tonnes*.

The Enriching Unit utilizes the property of deuterium atoms to concentrate in water at low temperatures and in hydrogen sulphide gas at high temperatures. There are three stages per unit, each having a hot and cold section. Deuterium enriched H_2S is transferred between the hot sections of the first, second and third stages, carrying with it increasing concentrations of deuterium. Finally, in the third stage, water in the cold section tower contains sufficient heavy water to be removed for final processing in the Finishing Unit. Figure 2 shows the flow of gas and water between the various stages of the enriching process. It should be noted that there are three first stage towers operated in parallel. The

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*Process information is based on Part I (Design Description), Bruce HWP Safety Report, Ontario Hydro, 1978.

H_2S is also contained in the piping and equipment of the Enriching Unit. The major H_2S carrying pipes are identified below. All carry H_2S in gaseous form under pressure:

3 x 1.3m (52 in)	lines carrying cold H_2S from top to bottom of the first stage towers
3 x 1.1m (42 in)	lines carrying cold H_2S from the top of the second stage tower to the centre of each first stage tower
3 x 1.1m (42 in)	lines carrying hot H_2S from the centre of each first stage tower to the bottom of the second stage tower
1 x 0.6m (24 in)	line carrying H_2S from the top of the hot third stage tower to the bottom of the cold third stage tower
1 x 0.6m (24 in)	line carrying H_2S from the top of the cold third stage tower to the centre of the second stage tower
1 x 0.6m (24 in)	line carrying hot H_2S from the centre of the second stage tower to the bottom of the hot third stage tower

The above piping, together with associated equipment, smaller interconnecting pipes and liquid lines, etc., are estimated to account for about 20% of the total H_2S inventory of the Enriching Unit (ref. Port Hawkesbury HWP Safety Analysis).

The H_2S storage area of a heavy water plant normally contains a significant inventory, stored under pressure in liquid form at saturation conditions (2720 kPa and 38°C). At Bruce HWP there are six 'bullet' tanks, each having a design capacity of 180 tonnes of H_2S. In an adjacent area

rail tank cars of liquid H_2S are unloaded. The maximum capacity of cars currently in use is 41 tonnes.

At the plant's H_2S recovery area, gas is stripped from depleted process water and waste streams and returned to the process. At Bruce HWP, the recovery unit consists of two stripping towers, although the largest contribution to the H_2S inventory in this area is a compressor suction tank having a capacity of 1700 kg.

The transfer of H_2S between the Enriching Units, Storage and Unloading Area, Recovery Area and flare stacks (used to burn H_2S which may be dumped in the event of a process upset) is primarily through a system of 0.05, 0.1, 0.15 and 0.3m lines (2, 4, 6 and 12 inch). These are suspended on pipe racks which, at Bruce HWP appear to be between 6 and 10 m above ground level. Line pressure is 2350 kPa during transfer operations with the exception of the return line from the recovery area which operates at 500 kPa. The pipes extend over considerable distances within the plant, as shown in the layout diagram of the Bruce HWP given in Figure 3. Although a definitive figure for the H_2S inventory contained within these lines does not appear to be available, it has been estimated at 0.7 tonnes for the Bruce plant, based on double lines of average diameter 0.1m following the dotted lines shown in the figure.

Table 2 summarizes the H_2S inventory for the Bruce HWP, as discussed above. Both the A and B plants are assumed to be operating at full capacity and the existing storage tanks are assumed full. A single tank car is included in the storage area inventory.

Although various design features and operating procedures are in place at heavy water plants to minimize the likelihood of such events, nonetheless it is possible that an H_2S release could be precipitated at any point in the containment system. Scenarios range from a catastrophic failure of an Enriching Unit tower or storage tank down to a minor leak at a valve stem or flange.

In the case of the Bruce HWP, the extent of H_2S containment and the inventories associated with the major elements of the system have been identified in Section 3.1.2. From Fig. 3, it is apparent that a release could occur from many points within a wide area inside the

The Enriching Unit towers and some pipework rise to about 110m above grade (108m for Bruce A and 114m for Bruce B), although most H_2S carrying lines and equipment are found close to ground level, approximately within the first 10m. The larger lines (0.6-1.3 m, or 24-52 inch diameter) carrying H_2S between different stages of the enriching process extend alongside the towers (see Section 3.1.2). In addition, manholes are located in the walls of the process towers to provide access during maintenance. These are 0.6m (24 in) in diameter and at various levels depending on the process stage. Figure 4 gives a diagrammatic representation of one of the two enriching units at Bruce HWP "A". Manhole locations are shown on the diagram. As indicated, there are up to seven manholes per tower at elevations ranging from 7.7 to 80.8 m above grade. At Bruce, all manholes are on the north side of the towers.

In the H_2S storage and unloading area, tanks and pipes are generally at or near ground level. At Bruce HWP, the 'bullet' storage tanks are arranged in a row, each one oriented in an east-west direction with a mass of pipework, mainly of small diameter, extending along the east side of the row. Tank-car unloading takes place at the north end of this area. Pipework in this area is estimated to be mostly 3-5m above grade, and may carry H_2S in either liquid or vapour form. The area is dyked to contain spills of liquid H_2S should this occur. Short of a catastrophic failure of a storage tank or tank car, the largest potential release in this area would be due to the failure of a tank manhole. These are normally of 0.6m (24 in) diameter and located on the top of each tank, approximately 4m above grade.

The two flare stacks at Bruce HWP are shown on Figure 3. The more southerly stack serves plant A only, while the other stack can serve either plant B or common services. Both stacks are 145m high. An emergency dump of H_2S to the flare stack would normally be ignited at the stack tip by the propane system and burn to SO_2. However, failure of the ignition system would result in the release of H_2S from the stack.

As previously noted, interconnecting pipework in a heavy water plant is carried on piperacks. At Bruce HWP, pipe elevations on these racks are about 8 to 10m above grade. Finally, potential gas releases in the H_2S recovery area would take place near ground level. The largest inventory in this area is in the compressor suction tank, located at grade, although the stripper towers themselves extend to some 21m above grade and must be considered a potential accidental source of H_2S.

3.1.4 Release Scenarios

Licencees of heavy water plants in Canada have concentrated, in their safety assessments, on certain H_2S release scenarios which are considered to be the worst credible. With the exception of the failure of a 0.6m (24 in.) manhole, catastrophic failures of the pressure envelope have not been addressed. As well, the larger pipe breaks are believed to autoignite to SO_2 and, thereafter, represent a reduced safety hazard to the public (see, for example, Ontario Hydro, 1980 and 1982). Table 3 summarizes the scenarios considered to date for the Bruce HWP, together with the assumed location of the release and the gas release rate. It is believed that similar conditions have been examined at Glace Bay, as well as the consequences of burning SO_2 releases for 0.05 through 0.6 m diameter breaks. A release for a stripper tower was also considered, assumed to take place 'at the top of a process tower'.

Although the above situations may be illustrative of credible initiating events, they do not cover the full range of possible cases. Table 4 has been assembled on the basis of what is conceivable without, admittedly, the benefit of an examination of the likelihood of the situations ever arising. As previously stated, such an examination is beyond the scope of the present study. The expanded list of scenarios presented in the table is intended solely to permit the specification of a modelling procedure which could, if required, handle the full range of cases. Not all specific cases of possible equipment failure have been included (e.g. stripper tower failure) Those excluded are believed to be of lesser severity and, because of similarities to other scenarios, would not expand the modelling requirements.

A phenomenon associated with the rapid expansion of vapours is the formation of supercooled vapour in so-called metastable states. This would occur at the low pressures found near the break in the pressure envelope and would result in increased flow through the opening. Restoration of thermodynamic equilibrium occurs irreversibly with an increase in entropy and pressure after the exit. In practice, it is unclear to what extent the thermal inertia of the equipment will offset this effect, thus reducing the flow rate to be closer to the ideal flow case suggested by equation (8) above. Data generated by AECL for the flow of a real gas, suggest that without accounting for thermal inertia, the initial flow rate from a failed manhole would be about 1650 kg/s, compared with 1100 kg/s for ideal flow. Nevertheless, for practical purposes, it is felt that equation (8), with use of a suitable discharge coefficient to account for the irreversibilities discussed above, is suitable for determination of gas flow rates in the present context. The choice of discharge coefficient should be the subject of further investigation and sensitivity analysis.

Under choked flow conditions, the time history of the discharge is controlled by the reservoir or pipe pressure, p_i. The time history of p_i has been shown to be governed by the equation (e.g. Allen, 1976)

$$p_i = p_{o_i} e^{-kt} \qquad (9)$$

where p_{o_i} is the initial reservoir pressure and k is a constant which depends on the reservoir volume, the size of the break and the reservoir temperature. For H_2S, Allen gives an equation for k as follows:

$$k = \frac{\alpha \; 2.72 \times 10^3 \; A_b}{\sqrt{T_i} \quad \bar{v}} \qquad (S^{-1}) \qquad (10)$$

where T_i is the reservoir temperature, $\bar{v}$ the effective volume, A_b the break area and α is an empirical factor to allow for friction. Allen presents values of α determined from experimental data collected at Glace Bay HWP, where blowdowns through emergency dump values were measured. Values ranged from 0.26 (0.05m or 2 in dia) to 0.64 (0.15 m or 6 in dia).

To establish the orders of magnitude of the release rates and the characteristic time constants of the blowdown curves, several of the scenarios given in Table 4 have been evaluated using the above equations. It is assumed that a single first stage tower of volume 5000m³ (including associated piping and equipment) is discharged through the break. The average tower temperature is taken at 353K (hot and cold sections), and the initial system pressure 2090 kPa. The time constant evaluated is the time required to reduce the pressure in the tower to the critical pressure (~ 200 kPa), at which point choked flow no longer exists at the break. Results are given in Table 6. In this evaluation, no credit is given for operator action. This will have the result of reducing the quantity of gas released and the release duration.

In the event of a discharge from an isolated length of pipe, the contents of a sufficiently long pipe would discharge in thermal equilibrium with its surroundings. The resulting isothermal flow problem has been discussed by Wilson (1979) with application to sour gas pipe lines. The process can be described by a double-

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LOCATION	QUANTITY (TONNES)	PHYSICAL STATE
Enriching Units (4) incl. interconnecting pipes and associated equipment	2160	Approx. 90% as gas at 2080 kPa Approx. 51% at 32°C and 39% at 128°C
H_2S storage and unloading area	897	Liquid at saturated conditions (2720 kPa, 38°C)
H_2S Recovery Area	2	Primarily gas
Interconnecting pipes	<1	Primarily gas at 2350 kPa.
TOTAL	3060	

TABLE 2

SUMMARY OF ESTIMATED H_2S INVENTORY

FOR BRUCE HWP (A AND B)

Molecular Weight (g/mole)	34.08
Melting Point (°C)	-82.9
Boiling Point (°C)	-61.8
Density (g/L at 0°C and 101.3 kPa)	1.539
Sound Speed (m/s)	289
Vapour pressure, (kPa at temp in °C)	1094 @0; 1875 @20; 3009 @40; 4509 @60; 6485 @80; 6988 @100
Solubility (in water, g/100g per 101.3 kPa at temp in °C)	4.95 @0; 8.77 @30; 13.2 @40; 17.8 @60; 22.8 @80; 24.7 @100
Heat of combustion (kJ/kg)	15,300
Ignition temp. (°C)	260
Flammable range	4-44% by volume in air

TABLE 5

PHYSICAL-CHEMICAL PROPERTIES OF H_2S

(from NRCC, 1981 and Weast, 1982)

SCENARIO	EMISSIONS	DURATION	ELEVATION	LOCATION	EFFECTIVE PHYSICAL EXTENT	DENSITY	NOTES
1. Catastrophic failure of Enriching Unit tower	Total tower H_2S inventory e.g. 120 tonnes	Few seconds	Ground level to ~ 110m	At rupture	Cloud 100's of meters, from Hardee & Lee (1975)	Neutrally buoyant cloud from Haddock & Williams (1978) Eqns (16) & (17)*	*Modified according to tower and ambient temperatures
2. a) Non-burning release from pipe breaks. 0.15-1.3m (6-52in) dia. b) burning release from same source	Initially 83.8-6290 kg/s H_2S depending on break size (single-ended breaks)	1000's to 10's of seconds depending on break size	Ground level to ~110m	10's of metres from break at end of jet phase, See eqns. (14) & (15)	Jet metres in diameter	a) Neutrally buoyant cloud of H_2S/air following jet b) Buoyant SO_2 / air cloud following jet	Single or double ended break. Gas jet horizontal or vertical.
3. a) Non-burning release from 0.6m (24in) manhole in enriching unit tower	Initially 1340 kg/s H_2S	100's of seconds	~7 to 80m above grade	100's of metres from break at end of jet phase see eqns. (14) & (15)	Jet 10's of metres in diamter	a) Neutrally buoyant cloud of H_2S/air following jet b) Buoyant SO_2/ air and cloud following jet	Jet horizontal
4. Non-burning release from pipe breaks. 0.05-0.1m (2-4in) dia.	9.3-37.3 kg/s (single-ended breaks)	Continuous	ground level to ~110m	10's of metres from break at end of jet phase see eqns. (14) & (15)	Jet metres in diameter	Neutrally buoyant cloud of H_2S/air following jet	Single or double ended break. Gas jet horizontal or vertical
5. Catastrophic failure of H_2S storage tank	Total H_2S inventory e.g. 144 tonnes	Few seconds	~ground level	At rupture	Cloud 100's of metres dia. From Hardee & Lee (1975)	Dense cloud from Haddock and William (1978) Eqns (18) & (19)*	*Modified according to storage and ambient temperatures

CONTINUED.....

TABLE 7

APPENDIX C

EFFECTS ON CONSEQUENCES DUE TO CHANGES IN REPORT INFO-102-1

1. INTRODUCTION

As a result of the peer review by Ontario Hydro of the first phase of the programme of probabilistic consequence assessments (Ref.1), two changes in the operating conditions at the Bruce HWP were identified which may affect the consequence predicted by the GASPROB code. These are:

a) a process tower operating pressure of 1825 kPa, rather than the value of 2030 kPa assumed in the derivation of consequences, and

b) a maximum inventory in any one liquid H2S storage tank of 144 tonnes, rather than 180 tonnes as assumed in the derivation of consequences (the latter figure represents the maximum design capacity).

The corresponding changes in the consequences given in Ref. 3 are discussed below in a semi-quantitative fashion. Further runs of the GASPROB code to determine the exact changes were not conducted.

2. EFFECTS OF CHANGE IN PROCESS TOWER OPERATING PRESSURE

The process tower operating pressure determines the flow rate of H2S through the postulated break in the pressure envelope, as well as the flow rate to the flare stack if the contents of the tower are dumped. The flow rates originally calculated assuming a tower pressure of 2030 kPa, and given in Appendix B to Ref 3, have been re-calculated with a pressure of 1825 kPa. This has been done for all the break scenarios considered in the consequence assessments. The results are shown in the attached tables.

The major effect of significance is a reduction in the initial gas flow rates (H2S or S02, for burning releases) by 10%. Since the mean gas concentrations experienced downwind of the plant are essentially directly proportional to the flow rate (the plume rise of a burning release is only weakly affected), concentrations are reduced by a corresponding amount. Thus, for any given combination of release scenario and weather condition, the probability of fatalities at a certain point downwind of the plant may be decreased. The size of this decrease will vary, depending on the

mean concentration level relative to the lethal level. For example, if the mean concentration originally calculated, based on a tower pressure of 2030 kPa was well above the lethal level for a 10 minute exposure or longer, a 10% reduction would have no effect on the probability of fatalities at the location considered (100%). Similarly, if the original mean concentration was well below the lethal level, the probability would again be unchanged (0%). At intermediate concentrations, it is necessary to consider the influence of the mean concentration on the probability of fatalities incorporating the so called "peak-to-mean" effect. An earlier report (Ref. 5) considers this effect in detail and provides an indication of the sensitivity of the probability of a lethal exposure to the mean concentration. The relevant figure from Ref. 3 showing this sensitivity is reproduced here as Figure C.1. It can be seen that a 10% reduction in the mean concentration can result in a reduction in the probability of exceeding the lethal threshold of some 25% (this can be greater where the mean concentration is low, but in this range the probabilities approach zero).

It is expected that the reduction in the probabilities of non-zero consequences would be substantially less than 25% since, at Bruce HWP, most of the predicted fatalities would occur at distances where the peak-to-mean effect is not significant. Under these circumstances, a change in the predicted consequences would only come about where the originally calculated mean concentration were 10% or less above the lethal level. This would only occur over a very limited area and affect relative small populations, if any. Thus, the net effect would be a small left-ward shift of the consequence histograms given in Ref. 3. Since the class intervals used in the histograms are quite wide, this shift may not be detectable in many cases.

3. EFFECT OF REVISED STORAGE TANK INVENTORY

As a result of this revision, the amount of H_2S released under the scenario of a catastrophic storage tank failure is reduced by 20%. This translates to a 20% reduction in the mean concentrations experienced downwind of the plant, since any changes in the near-field behaviour of the heavier- than-air gas cloud would not significantly affect these concentrations (see Ref.3).

Although, as shown in Figure C.1., a 20% reduction in mean concentration can have a major influence on the "peak-to-mean" effect, only a small change in the consequence histogram is expected for the same reasons given in section 2 above.

REVISED BLOWDOWN FLOW RATES OF H2S

(revised from Appendix B of AECB INFO-102-3)

H2S BLOWDOWN: 1300mm Single-ended, No Isolation

Effective Diameter: 1.3 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0102628 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	4776.9050
20	1486.3505	20.065733	3890.4962
40	1210.5414	16.342309	3168.5706
60	985.91176	13.309808	2580.6065
80	802.96468	10.840023	2101.7457
100	653.96550	8.8285342	1711.7430
150	391.47210	5.2848734	1024.6712
200	234.34020	3.1635927	613.38132
250	140.27904	1.8937670	367.17789
300	83.972827	1.1336331	219.79738

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0416059 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	0	0	0
150	0	0	0
170	0	0	0
190	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0420213 (s**-1)
Initial Pressure: (kPa) at time: (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

H2S BLOWDOWN: 1300mm Single-ended, Isolation

Effective Diameter: 1.3 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0102628 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	4776.9050
20	1486.3505	20.065733	3890.4962
40	1210.5414	16.342309	3168.5706
60	985.91176	13.309808	2580.6065
80	802.96468	10.840023	2101.7457
100	653.96550	8.8285342	1711.7430
130	480.66492	6.4889764	1258.1318

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0416059 (s**-1)
Initial Pressure: 480.66492 (kPa) at time: 130 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	480.66492	6.4889764	1258.1318
150	209.14984	2.8235228	547.44598
170	91.006549	1.2285884	238.20802
190	39.599322	0.5345908	103.65052

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0420213 (s**-1)
Initial Pressure: (kPa) at time: (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

H2S BLOWDOWN: 600mm Manway, No Isolation

Effective Diameter: 0.6 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0021861 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	1017.5655
100	1466.6252	19.799440	817.74647
200	1178.6243	15.911429	657.16580
300	947.17821	12.786905	528.11832
500	611.70813	8.2580598	341.07021
700	395.05431	5.3332332	220.27050
900	255.13460	3.4443171	142.25544
1100	164.77143	2.2244143	91.871637
1300	106.41294	1.4365748	59.332686

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0088628 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	0	0	0
150	0	0	0
170	0	0	0
190	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0
	0	0	0

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0092782 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
190	0	0	0
250	0	0	0
300	0	0	0
350	0	0	0
400	0	0	0
450	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

H2S BLOWDOWN: 600mm Manway, Isolation

Effective Diameter: 0.6 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0021861 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	1017.5655
100	1466.6252	19.799440	817.74647
200	1178.6243	15.911429	657.16580
300	947.17821	12.786905	528.11832
400	761.18106	10.275944	424.41186
490	625.22830	8.4405820	348.60865

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0088628 (s**-1)
Initial Pressure: 625.22830 (kPa) at time: 490 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
490	625.22830	8.4405820	348.60865
520	479.25486	6.4699407	267.21822
550	367.36217	4.9593893	204.83019

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0092782 (s**-1)
Initial Pressure: 367.36217 (kPa) at time: 550 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
550	367.36217	4.9593893	204.83019
650	145.26019	1.9610126	80.992753
700	91.342464	1.2331232	50.929833

H2S BLOWDOWN: 150mm Double-ended, Slow Isolation, No Dump

Effective Diameter: 0.2121 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0002731 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	127.15728
50	1800.2411	24.303255	125.43220
100	1775.8181	23.973544	123.73052
150	1751.7264	23.648307	122.05193
200	1727.9616	23.327482	120.39611
250	1704.5192	23.011010	118.76276
300	1681.3948	22.698831	117.15156
350	1658.5842	22.390887	115.56222
385	1642.8011	22.177815	114.46253
475	1602.9023	21.639181	111.68257

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0011075 (s**-1)
Initial Pressure: 1602.9023 (kPa) at time: 475 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
475	1602.9023	21.639181	111.68257
535	1499.8497	20.247971	104.50236
600	1395.6724	18.841578	97.243789
800	1118.3708	15.098005	77.922735
1000	896.16532	12.098231	62.440519
1200	718.10913	9.6944732	50.034414
1500	515.10281	6.9538879	35.889903
1750	390.52317	5.2720629	27.209789
2000	296.07361	3.9969938	20.628995
2500	170.17881	2.2974140	11.857246

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0015229 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

H2S BLOWDOWN: 150mm Double-ended, Fast Isolation, No Dump

Effective Diameter: 0.2121 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0002731 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	127.15728
20	1815.0558	24.503253	126.46442
40	1805.1658	24.369739	125.77533
60	1795.3298	24.236952	125.09000
80	1785.5473	24.104888	124.40840
100	1775.8181	23.973544	123.73052
120	1766.1419	23.842916	123.05633
130	1761.3236	23.777869	122.72062

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0011075 (s**-1)
Initial Pressure: 1761.3236 (kPa) at time: 130 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	1761.3236	23.777869	122.72062
200	1629.9338	22.004107	113.56600
400	1306.0875	17.632182	91.001943
600	1046.5852	14.128900	72.921061
800	838.64261	11.321675	58.432611
1000	672.01542	9.0722082	46.822825
1300	482.03959	6.5075345	33.586216
1600	345.76910	4.6678829	24.091539
1900	248.02168	3.3482927	17.280966
2200	177.90703	2.4017450	12.395712

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0015229 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	

H2S BLOWDOWN: 150mm Double-ended, Slow Isolation with Dump

Effective Diameter: 0.2121 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0002731 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	127.15728
475	1602.9023	21.639181	111.68257

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0011075 (s**-1)
Initial Pressure: 1602.9023 (kPa) at time: 475 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
475	1602.9023	21.639181	111.68257
535	1499.8497	20.247971	104.50236

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0015229 (s**-1)
Initial Pressure: 1499.8497 (kPa) at time: 535 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s) at break	Q(kg/s) to stack
535	1499.8497	20.247971	104.50236	39.200225
600	1358.4916	18.339637	94.653207	35.505675
700	1166.5874	15.748930	81.282240	30.490048
800	1001.7921	13.524194	69.800092	26.182941
900	860.27629	11.613729	59.939943	22.484268
1000	738.75134	9.9731431	51.472665	19.308080
1200	544.77722	7.3544925	37.957475	14.238353
1400	401.73494	5.4234216	27.990971	10.499785
1900	187.60363	2.5326491	13.071325	4.9032277
2400	87.607826	1.1827056	6.1040948	2.2897270

H2S BLOWDOWN: 150mm Double-ended, Fast Isolation with Dump

Effective Diameter: 0.2121 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0002731 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	127.15728
130	1761.3236	23.777869	122.72062

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0011075 (s**-1)
Initial Pressure: 1761.3236 (kPa) at time: 130 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	1761.3236	23.777869	122.72062
190	1648.0859	22.249160	114.83075

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0015229 (s**-1)
Initial Pressure: 1648.0859 (kPa) at time: 190 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s) at break	Q(kg/s) to stack
190	1648.0859	22.249160	114.83075	43.074543
300	1393.8827	18.817416	97.119089	36.430660
400	1196.9790	16.159217	83.399784	31.284367
600	882.68799	11.916287	61.501483	23.070023
900	558.96962	7.5460899	38.946333	14.609287
1200	353.97223	4.7786251	24.663094	9.2514544
1500	224.15590	3.0261047	15.618112	5.8585616
1700	165.29923	2.2315396	11.517261	4.3202777

H2S BLOWDOWN: 50mm Double-ended, Slow Isolation, No Dump

Effective Diameter: 0.0707 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0000303 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	14.128586
100	1819.4687	24.562828	14.085765
200	1813.9542	24.488382	14.043074
500	1797.5109	24.266397	13.915775
1000	1770.4359	23.900885	13.706169
2000	1717.5032	23.186294	13.296380
3470	1642.5518	22.174449	12.716129
3530	1639.5630	22.134101	12.692991

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0001230 (s**-1)
Initial Pressure: 1639.5630 (kPa) at time: 3530 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
3530	1639.5630	22.134101	12.692991
5000	1368.2538	18.471427	10.592599
6000	1209.8277	16.332674	9.3661129
8000	945.88254	12.769414	7.3227308
10000	739.52165	9.9835423	5.7251484
15000	399.70087	5.3959618	3.0943608
20000	216.03260	2.9164402	1.6724578

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0005384 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	

H2S BLOWDOWN: 50mm Double-ended, Fast Isolation, No Dump

Effective Diameter: 0.0707 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0000303 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	14.128586
20	1823.8924	24.622547	14.120012
40	1822.7854	24.607604	14.111442
60	1821.6792	24.592669	14.102878
80	1820.5736	24.577744	14.094319
100	1819.4687	24.562828	14.085765
120	1818.3645	24.547921	14.077217
130	1817.8126	24.540470	14.072944

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0001230 (s**-1)
Initial Pressure: 1817.8126 (kPa) at time: 130 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	1817.8126	24.540470	14.072944
200	1802.2212	24.329986	13.952240
400	1758.4072	23.738498	13.613046
600	1715.6584	23.161389	13.282098
1000	1633.2534	22.048921	12.644144
1500	1535.7905	20.733172	11.889616
2000	1444.1437	19.495940	11.180115
3000	1276.9304	17.238561	9.8856019
4000	1129.0784	15.242558	8.7409767
6000	882.75011	11.917126	6.8339790

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0005384 (s**-1)
Initial Pressure: 0 (kPa) at time: 0 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	
0	0	0	

H2S BLOWDOWN: 50mm Double-ended, Slow Isolation with Dump

Effective Diameter: 0.0707 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0000303 (s**-1)
Initial Pressure: 1825 (kPa)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	14.128586
100	1819.4687	24.562828	14.085765
200	1813.9542	24.488382	14.043074
500	1797.5109	24.266397	13.915775
1000	1770.4359	23.900885	13.706169
2000	1717.5032	23.186294	13.296380
3470	1642.5518	22.174449	12.716129
3530	1639.5630	22.134101	12.692991

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0001230 (s**-1)
Initial Pressure: 1639.5630 (kPa) at time: 3530 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
3530	1639.5630	22.134101	12.692991
3590	1627.5020	21.971277	12.599618

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0005384 (s**-1)
Initial Pressure: 1627.5020 (kPa) at time: 3590 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s) at break	Q(kg/s) to stack
3590	1627.5020	21.971277	12.599618	42.536559
4000	1305.0959	17.618795	10.103650	34.110121
4500	997.04953	13.460168	7.7188499	26.058988
5000	761.71238	10.283117	5.8969423	19.908192
6000	444.56941	6.0016871	3.4417192	11.619311
7000	259.47059	3.5028530	2.0087413	6.7815499
7500	198.22682	2.6760621	1.5346109	5.1808766

H2S BLOWDOWN: 50mm Double-ended, Fast Isolation with Dump

Effective Diameter: 0.0707 (m)

Initial Phase:
Effective Volume: 15000 (m**3) K = 0.0000303 (s**-1)
Initial Pressure: 1825 (kPa)

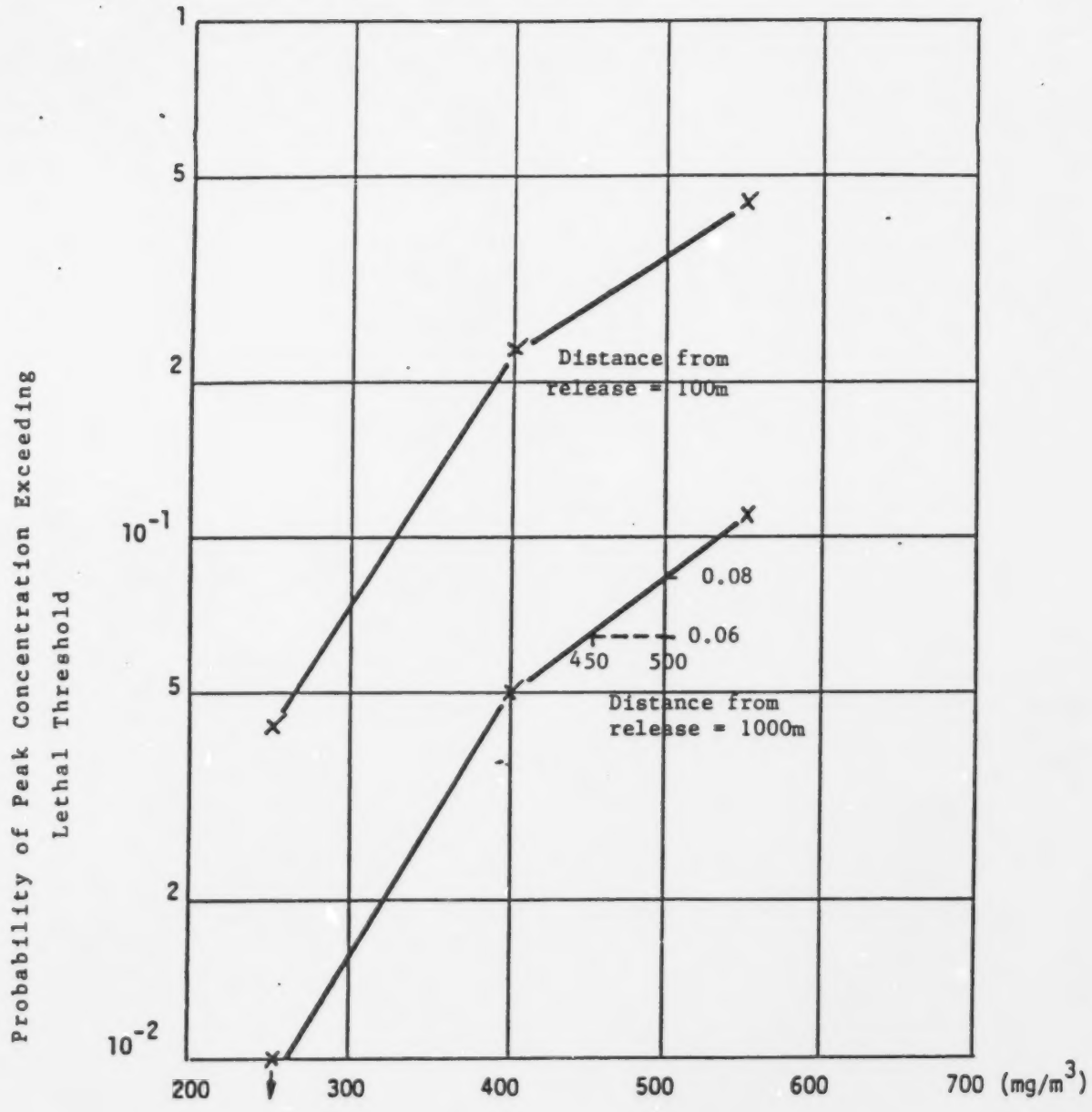
T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
0	1825	24.6375	14.128586
50	1822.2322	24.600135	14.107160
100	1819.4687	24.562828	14.085765
130	1817.8126	24.540470	14.072944

Post Isolation:
Effective Volume: 3700 (m**3) K = 0.0001230 (s**-1)
Initial Pressure: 1817.8126 (kPa) at time: 130 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s)
130	1817.8126	24.540470	14.072944
190	1804.4403	24.359945	13.969420

Post Dump:
Effective Volume: 3700 (m**3) K = 0.0005384 (s**-1)
Initial Pressure: 1804.4403 (kPa) at time: 190 (s)

T(s)	P(kPa)	Rho(kg/m3)	Q(kg/s) at break	Q(kg/s) to stack
190	1804.4403	24.359945	13.969420	47.161037
400	1611.5127	21.755421	12.475834	42.118660
800	1299.2513	17.539892	10.058402	33.957364
1200	1047.4965	14.141202	8.1093948	27.377475
1600	844.52403	11.401074	6.5380445	22.072566
2000	680.88135	9.1918982	5.2711733	17.795584
2500	520.17050	7.0223018	4.0269995	13.595229
3000	397.39281	5.3648029	3.0764925	10.386299
4000	231.93621	3.1311389	1.7955786	6.0619086
5000	135.36835	1.8274727	1.0479800	3.5380010



MODEL SENSITIVITY TO LONG-TERM CONCENTRATION MEAN (from Ref. 5)

FIGURE C1